

WEST

Generate Collection

Print

L6: Entry 1 of 2

File: JPAB

Feb 2, 1993

PUB-NO: JP405024976A

DOCUMENT-IDENTIFIER: JP 05024976 A

TITLE: METHOD FOR DOPING SEMICONDUCTOR AND APPARATUS THEREFOR

PUBN-DATE: February 2, 1993

INVENTOR-INFORMATION:

NAME

COUNTRY

NAKAGAWA, KATSUMI

TAKABAYASHI, MEIJI

TAKEUCHI, EIJI

ASSIGNEE-INFORMATION:

NAME

COUNTRY

CANON INC

APPL-NO: JP03186489

APPL-DATE: July 25, 1991

US-CL-CURRENT: 118/723MP; 118/723VE

INT-CL (IPC): C30B 25/06; C30B 31/20; H01L 21/22; H01L 29/784; H01L 31/04

ABSTRACT:

PURPOSE: To provide a doping apparatus capable of obtaining a p type or n type semiconductor having excellent properties, capable of obtaining properties uniform over a large area and capable of manufacturing a large sized semiconductor device at a low cost.

CONSTITUTION: The inside of a chamber 101 is provided with a pair of electrodes, i.e., an anode 103 and a cathode 104. The anode 103 is set with a sample 105. The sample 105 can be heated by a heater 106. The cathode 104 is connected to a power source 108 for generating a plasma 107 between the anode 103 and the cathode 104. A target 109 is set on the cathode 104. An inert gas is introduced into the chamber 101 from a cylinder 110. Furthermore, the inside of the chamber 101 is provided with light sources 112 and 113 of ultraviolet light as well, and irradiation on the surface of the sample 105 is permitted as occasion demands.

COPYRIGHT: (C)1993, JPO&Japio

WEST**End of Result Set**

Generate Collection

Print

L6: Entry 2 of 2

File: DWPI

Feb 2, 1993

DERWENT-ACC-NO: 1993-080266
DERWENT-WEEK: 199310
COPYRIGHT 2002 DERWENT INFORMATION LTD

TITLE: Doping of semiconductor - comprises irradiating surface with UV beam while sputtering target contg. dopant element

PATENT-ASSIGNEE:

ASSIGNEE

CODE

CANON KK

CANO

PRIORITY-DATA: 1991JP-0186489 (July 25, 1991)

PATENT-FAMILY:

PUB-NO

PUB-DATE

LANGUAGE

PAGES

MAIN-IPC

JP 05024976 A

February 2, 1993

012

C30B025/06

APPLICATION-DATA:

PUB-NO

APPL-DATE

APPL-NO

DESCRIPTOR

JP05024976A

July 25, 1991

1991JP-0186489

INT-CL (IPC): C30B 25/06; C30B 31/20; H01L 21/22; H01L 29/784; H01L 31/04

ABSTRACTED-PUB-NO: JP05024976A

BASIC-ABSTRACT:

While depositing a dopant onto the surface of a semiconductor through sputtering with a target contg. the dopant element, the semiconductor surface is irradiated with UV beam contg. wavelengths 300nm and below, for the doping of semiconductor. The simultaneous irradiation can be replaced by a post irradiation.

Appts. includes: chamber (101); vacuum pump (102); anode (103); cathode (104); specimen (105); heater (106); plasma (107); power source (108); target (109); inert gas holder for Ar (110); mass-flow controller (111); Hg lamps (112,113) and butterfly valve (114).

ADVANTAGE - The doping is effected without damaging the dope semiconductor. Because of no requirement for high temp. post treatment, p- or n-type domains of good characteristics can be formed whether the semiconductor be monocrystalline, polycrystalline or amorphous.

CHOSEN-DRAWING: Dwg.1/9

TITLE-TERMS: DOPE SEMICONDUCTOR COMPRISE IRRADIATE SURFACE ULTRAVIOLET BEAM SPUTTER TARGET CONTAIN DOPE ELEMENT

DERWENT-CLASS: L03 U11 U12 X15

CPI-CODES: L04-C02;

EPI-CODES: U11-C02J4; U11-C02J7; U12-A02A3; X15-A02;

SECONDARY-ACC-NO:

(19)日本特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平5-24976

(43)公開日 平成5年(1993)2月2日

(51)Int.Cl. ⁵	識別記号	序内整理番号	F I	技術表示箇所
C 3 0 B 25/06		9040-4G		
31/20		7821-4G		
H 0 1 L 21/22	E	9278-4M	H 0 1 L 29/ 78	3 1 1 F
		9056-4M	31/ 04	B
		7376-4M		

審査請求 未請求 請求項の数 4(全 12 頁) 最終頁に続く

(21)出願番号 特願平3-186489

(22)出願日 平成3年(1991)7月25日

(71)出願人 000001007

キャノン株式会社

東京都大田区下丸子3丁目30番2号

(72)発明者 中川 克己

東京都大田区下丸子3丁目30番2号 キャ
ノン株式会社内

(72)発明者 高林 明治

東京都大田区下丸子3丁目30番2号 キャ
ノン株式会社内

(72)発明者 竹内 栄治

東京都大田区下丸子3丁目30番2号 キャ
ノン株式会社内

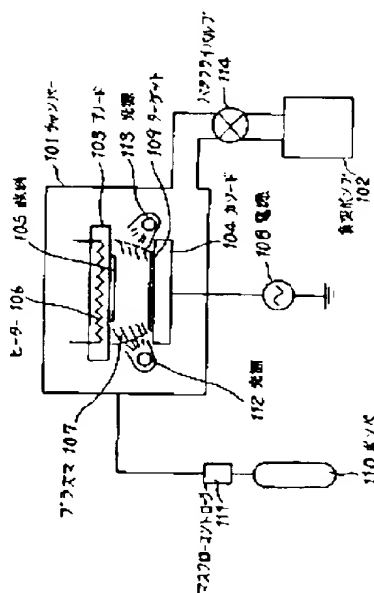
(74)代理人 弁理士 若林 忠

(54)【発明の名称】 半導体のドーピング方法及び装置

(57)【要約】

【構成】 チャンバー101の中には、アノード103及びカソード104の1対の電極が設けられている。アノード103には試料105がセットされている。試料105はヒーター106によって加熱することができる。カソード104はアノード103、カソード104間にプラズマ107を生起するための電源108に接続されている。カソード104の上にはターゲット109がセットされている。チャンバー101には、ポンプ110から不活性ガスが導入される。またチャンバー101内にはさらに紫外光の光源112、113が設けられていて、試料105の表面を随時照射できるようになっている。

【効果】 特性の優れたp型またはn型の半導体を得ることができ、大面積にわたって均一な特性が得られ、大型の半導体デバイスを低コストで製造できる。



(2)

特開平5-24976

1

【特許請求の範囲】

【請求項1】 トーバント元素を含有するターゲットを用いて、スパッタリング法により半導体の表面にトーバントを堆積させつつ、少なくとも波長300nm以下の成分を含む紫外光を前記半導体の表面に作用させて、前記半導体にドーピングを行う半導体のドーピング方法。

【請求項2】 トーバント元素を含有するターゲットを用いて、スパッタリング法により該表面にトーバントを堆積した後、少なくとも波長300nm以下の成分を含む紫外光を該表面に作用させて、前記半導体にドーピングを行う半導体のドーピング方法。

【請求項3】 半導体がセツトされる真空排気可能なチャンバーと

前記チャンバーの内部に設けられたアノードと表面にトーバント元素を含有するターゲットがセツトされたカソードと

該カソードに電力を供給する電源と、

前記半導体の表面に少なくとも波長300nm以下の成分を含む紫外光を照射する光源と、

前記チャンバーに少なくとも不活性ガスを供給するためのラインとを備えた半導体のドーピング装置。

【請求項4】 ターゲットに対向する位置と紫外光を照射する光源に対向する位置の間に半導体を搬送する手段を備えた請求項3記載の半導体のドーピング装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、高性能な太陽電池の液晶ディスプレイのアクティブマトリクス回路等の大面積半導体デバイスの量産に好適な半導体のドーピング方法及びドーピング装置に関するものである。

【0002】

【従来の技術】最近の半導体デバイス技術の流れとして、半導体メモリやイメージセンサーに代表される微細化、集積化の方向と共に、太陽電池や液晶ディスプレイのアクティブマトリクス回路に代表される大面積化の方向がある。大面積半導体デバイスにおいては、単位面積あたりの製造コストを極力下げる必要がある。そのため半導体材料として単結晶シリコンウェハーと共に、ガラス、金属、セラミックス等の廉価な基板上に堆積されたアモルファスや多結晶の半導体薄膜が用いられ始めている。しかしデバイス製造コストを下げるためには、他の各製造プロセスについても低コスト化が要求される。また製造されたデバイスは30cm角あるいはそれ以上の大面積にわたって特性が均一でなくてはならない。すなわち大面積デバイスにはそれにふさわしいプロセス技術が開発されなくてはならない。

【0003】各製造プロセスの中でも大面積化の観点から最も重要な技術としてドーピング技術が挙げられる。

【0004】半導体のドーピング技術として最も一般的に用いられてきたのは熱拡散法である。熱拡散法は半導

2

体表面に塗布または堆積した膜の中に含まれるドーバント原子を通常1000℃以上の高温で半導体中に拡散しドーバントとして活性化する技術である。この方法は比較的容易に大面積デバイスに適用できるが、高温を用いるため薄膜半導体を用いるに際し使用可能な基板に制約を受ける。また処理に長時間（通常数時間程度）を要し製造のスループットが良くない。

【0005】また他の一般的なドーピング技術としてイオンインプラネーション法がある。この方法では真空中でイオン化したドーバント原子イオンのビームから、質量分析の手段により不純物を取り除いた後、電界で加速して半導体中に打ち込み、通常800℃以上の温度で数時間程度アニールしてドーバントを活性化する方法である。この方法ではドーバントの制御がし易いが、大面積にわたりビームを走査する必要がありやはり製造のスループットが良くない。また装置が大きくなりなりやばりコスト面で不利となる。

【0006】一方、熱CVDやプラズマCVD等の方法で気相から堆積する薄膜半導体の場合には、薄膜の堆積時に気相中にドーバントを含むガスを混合して薄膜半導体中にドーバント原子を導入する方法がある。この方法では比較的大面積化も容易で、スループットも熱拡散法やイオンインプラネーション法に比べるとよいが、形成されたn型またはp型の半導体の特性は必ずしも十分ではなく半導体デバイスへの応用には十分なことが多かった。よく知られた例としては、熱CVDにより多結晶Siを堆積する際、原料のモノシラン（SiH₄）にフォスフィン（PH₃）を混合してn型にしようとする。特に高濃度ではSiの結晶粒が小さくなりn型Siとしての特性が、熱拡散法やイオンインプラネーション法でn型にする場合に比べて劣ったものとなる。またプラズマCVD法でアモルファスシリコン（a-Si）を堆積する際、原料のSiH₄にシオラン（B₂H₆）を混合してp型にしようとする。光学的バンドギャップ（E_g）が低下し、局在準位が増加してp型半導体としての特性は劣ったものとなる。

【0007】その理由としては、ドーバントを含むガスが気相中に混合されると、半導体を構成する主成分の元素（Si等）を含むガスの反応に影響を及ぼし、半導体の堆積のプリカーサー（堆積反応の前駆体）を変化させるためと考えられる。

【0008】また堆積によりドーピングを行うと、一般には基板上の特定の場所に選択的にn型やp型の半導体領域を形成することができない。このため特に液晶ディスプレイへの応用においてはプロセスが複雑化する。このような観点からいくつかの提案がなされている。

【0009】M.B. SpitzerとS.N. Bunkerはp型単結晶Siに質量分析を行わずにリン（P）のイオンインプラネーションを行い、pn接合をもつ変換効率15%の太陽電池を作った（16th IEEE Photovoltaic Conf. San

(3)

特開平5-24976

3

Sheen, 1982p.711-). H. Itoh等も同様な方法で反射防止層無しで変換効率10%の太陽電池を作った(Proc. 3rd PVSEC in Japan ('82) p.7-). 質量分析を行わないイオンインプラレーション法では、装置は比較的簡単となり製造のスループットも向上する。しかし太陽電池への応用上十分なほどの大面積の処理は困難である。また彼らの実験ではイオンを打ち込んだ後、550℃または600℃以上でアニールを行っており、製造のスループットが低いばかりでなく、薄膜半導体への応用に対して制約が多い。

【0010】また、S.D. Westbrook等は、酸素(B)を含むガスをグロー放電で分解し、さらに電界を印加することにより酸素イオンを加速し、n型単結晶Siに打ち込んだ後、550℃以上でアニールを行って、変換効率19%もの太陽電池を作っている(Appl. Phys. Lett., Vol. 50 ('87) p.469-). 一方、吉田、湖恒、平尾は同様の装置を用いてリンのa-Siへのドーピングを行い薄膜トランジスタ(TFT)を作っている(IEEE Elec. Device Lett., Vol. 9 (1988) p.90-). これらの方法では大面積化がし易く、製造のスループットも比較的良好。また後者において示されているように、半導体面の特定の場所に選択的にp型またはn型の領域を形成することができる。しかし質量分析を行わないためドーパントイオン以外に各種の不必要なイオンも高速で打ち込まれることとなる。したがって十分な温度でアニールすることが困難なa-Siの場合には特にイオンによるダメージが取り除けにくく、a-Si太陽電池への応用に当たっての障害になっていた。またイオン以外の中性のドーパント原子については制御ができず、これらのドーパント原子が装置の各部に拡散し易い。特にa-Si太陽電池では通常p-i-n接合を用いており、少なくともn型、i型、p型の3層から、さらに複数のp-i-n接合を積層したタンデム型a-Siセルでは6層、9層からなる。これらのドーパントは隣接する導電型の異なる半導体層(特にi層)に侵入するとデバイスの特性に悪影響を与え易い。中でもa-Si太陽電池の生産を目的として長尺の帯状基板に連続堆積を行うロールトゥロール装置では、隣接する成膜室へのドーパントの拡散が起こり易い。

【0011】このように高性能なa-Si太陽電池を量産するためには、大面積へのドーピング技術をさらに改善する必要があった。また結晶半導体太陽電池や液晶ディスプレイの場合にも製造のスループットのよいドーピング技術の開発が望まれていた。

【0012】

【発明が解決しようとする課題】本発明は、このような現状に鑑みなされたものであって、半導体デバイスの製造において、ドーパントの不要な拡散が少ない簡単な装置で、特性の優れたp型またはn型の半導体を、大面積にわたり均一性よく、短い処理時間で製造する方法及び

4

この方法を実施するための装置を提供し、特に高性能な太陽電池や液晶ディスプレイのような大面積の半導体デバイスの低コストでの製造を可能とし、これらのデバイスの普及に寄与することを目的とする。

【0013】

【課題を解決するための手段】本発明は、半導体の表面にスパッタリング法でドーパント層を堆積するにあたり、半導体の表面に紫外光を照射して、その作用でドーパントを活性化することによって、特性の良好なp型またはn型の半導体の領域を形成することを主旨としている。

【0014】すなわち、本発明の半導体のドーピング方法は、ドーパント元素を含有するターゲットを用いて、スパッタリング法により半導体の表面にドーパントを堆積させつつ、少なくとも波長300nm以下の成分を含む紫外光を前記半導体の表面に作用させて、前記半導体にドーピングを行うものである。

【0015】また、本発明の半導体のドーピング方法は、ドーパント元素を含有するターゲットを用いて、スパッタリング法により該表面にドーパントを堆積した後、少なくとも波長300nm以下の成分を含む紫外光を該表面に作用させて、前記半導体にドーピングを行うものである。

【0016】一方、本発明の半導体のドーピング装置は、半導体がセットされる真空排気可能なチャンバーと、前記チャンバーの内部に設けられたアノードと、表面にドーパント元素を含有するターゲットがセットされたカソードと、該カソードに電力を供給する電源と、前記半導体の表面に少なくとも波長300nm以下の成分を含む紫外光を照射する光源と、前記チャンバーに少なくとも不活性ガスを供給するためのラインとを備えたものである。

【0017】さらに、本発明の半導体のドーピング装置は、ターゲットに対向する位置と紫外光を照射する光源に対向する位置の間に半導体を搬送する手段を備えたものとしてすることができる。

【0018】

【作用】図1は本発明のドーピング方法を実施するのに好適な本発明のドーピング装置の実施態様を示す概略構成図である。

【0019】真空ポンプ102によって真空排気可能なチャンバー101の中には、アノード103及びカソード104の1対の高極が設けられている。アノード103には試料105がセットされている。

【0020】試料としては単結晶或多結晶の半導体ウェハー、ガラスや金属等の基板上に堆積された多結晶やアモルファスの半導体薄膜が用いられる。これらの半導体は目的に応じて予めドーピングされていてもよいし、ドーピングされていなくてもよい。試料105はヒーター106によって所望の温度に加熱することができる。カ

(4)

特開平5-24976

5

ソート104はアソート103、カソート104間にプラスマ107を生起するための電極108に接続されている。カソート104の上にはターゲット109がセットされている。ターゲットの材料としてはB, Al, Ga, In, Tl, Fe, As, Sb, Bi等が用いられる。電極108としては直流電極でもよいが高周波電極でもよい。特にターゲット材料が高抵抗な場合には、例えば13.56MHz等のラジオ周波数の電極が好適に使用できる。チャンパー101にはポンプ110からAr等の不活性ガスが導入される。不活性ガスの流量はマスフローコントローラー111によって調整される。そしてマスフローコントローラー111及びバタフライバルブ114の開度によってチャンパー101内の圧力が調整される。またチャンパー101にはさらに紫外光の光源として水銀灯112, 113（以降光源112, 113と記す）が設けられていて、試料105の表面を随時照射できるようにしている。

【0021】実験1

本発明の効果を確認するため次のような実験を行った。真面に全高極をエッチングしたp型のSiウェハー（比抵抗 $10\Omega\cdot\text{cm}$ ）を試料105とし図1のトーピング装置にセットした。一旦チャンパー101内を 10^{-5}Torr まで排気した後Arを 5 sccm 流し、バタフライバルブ114を調整して圧力を 10^{-3}Torr とした。次いで、基板温度が 100°C となるようヒーター106の電流を調整した。ターゲット109としては純度99.9%のPの単体のプレートを用いた。次いで光源112, 113を点灯した。この状態で電極108から反射電力が極小となるよう不図示の整合回路を調整しつつ、 200W の高周波電力を供給したところ、プラズマ107が生起された。この状態で100秒経過したところで電極108、光源112, 113及びヒーター106への電力の供給を止めた。試料が冷却した後、チャンパー101内より取り出して1cm角に切り出し試料1Aとした。

【0022】次に比較のために、光源112, 113を点灯しない他は前記と全く同じ工程にて試料1Bを作った。

【0023】次に試料1A, 1Bの裏面及び表面に導線を銀ペーストで固着した。まず両試料の暗での電圧電流特性を測定した。試料1Aでは1Vにおける整流比が 3×10^4 倍であった。それに対し試料1Bでは整流比は50倍しかとれなかった。さらにエアマス（AM）1.5のソーラーシミュレーターのもとでの両試料の太陽電池特性をみた。試料1Aでは変換効率（ η ）が9.3%と反射防止膜のない太陽電池として良好な特性が得られた。一方試料1Bでは変換効率（ η ）が2.7%と太陽電池としての機能は不十分であった。

【0024】実験2

図1で光源112, 113を点灯しない以外は実験1と

6

同様の手順でスパッタリングを行った後、光源112, 113を10分間点灯し、試料2Aを作った。また光源112, 113を点灯せず50秒間スパッタリングを行い、次いで5分間紫外光を照射し、再び同じ条件でスパッタリングと紫外光照射を繰り返し試料2Bを作った。

【0025】暗での1Vでの整流比は試料2Aでは 2×10^4 倍、試料2Bでは 1×10^4 倍であった。またAM1.5での太陽電池特性は試料2Aの変換効率（ η ）が7.8%、試料2Bの変換効率（ η ）が8.5%であった。

【0026】実験3

本発明がアモルファス半導体に対しても効果的であることを示すため図2に示すような太陽電池を作った。市販の高周波容量結合型グロー放電装置に厚さ1mmのステンレスの基板201をセットし、この上にa-Siのn型半導体層202、次いでa-Siのp型半導体層203を堆積した。n型半導体層202の作成条件は原料ガスとして5%のPH₃を混合したSiH₄を 5 sccm 、圧力 0.5Torr 、放電電力50W、基板温度 250°C とし、膜厚は200Åである。p型半導体層203の作成条件は原料ガスとしてSiH₄を 20 sccm 、圧力 0.5Torr 、放電電力100W、基板温度 250°C とし、膜厚は4000Åである。こうして試料を、図1の装置にセットした。ターゲット109として純度99.9%のBの単体のプレートを用いた。

【0027】トーピング条件としてはAr 5 sccm 、圧力 10^{-3}Torr 、基板温度 200°C 、放電電力200Wとし、光源112, 113を点灯しつつ50秒放電を継続しp型領域204を作成した。

【0028】試料が冷却した後、チャンパー101から取り出して、市販の抵抗加熱型真空蒸着装置にセットしてInとSnの合金を酸素雰囲気中で蒸着し、ITO（In₂O₃+SnO₂）層の透明電極205を厚さ700Å堆積し試料3Aとした。図2でn型半導体層202を厚さ200Åのp型a-Si層とした試料を、図1のトーピング装置にセットし、Pのターゲットを用い、前記と同様のトーピング条件でF型領域204を形成した。同様に透明電極205を形成し試料3Bとした。

【0029】両試料3A, 3Bを実験1と同様な手順で評価した。1Vでの整流比は試料3Aが 1×10^4 倍、試料3Bが 8×10^4 倍であった。また太陽電池としての変換効率（ η ）は試料3Aが8.5%、試料3Bが7.8%であり、いずれも優れた特性を示した。

【0030】トーピングの機構について

以上の実験結果に基づいて本発明のトーピング法の機構について次のように推測することかできる。スパッタリング法においては、放電のプラズマ中にAr等のイオンが存在するが、これらのイオンは負にバイアスされているカソート104上のターゲット109をたたく、その

(5)

特開平5-24976

7

結果反映してくるターゲットの構成原子が試料105上に堆積する。ドーパント原子は中性なので電界によって加速されることがないため、一般には試料の内部まで侵入しにくいであろう。しかし試料面に紫外光が照射されると、紫外光のフォtonsのエネルギーにより、半導体を構成するSi等の原子相互の結合を緩めるために、ドーパントの原子が試料の奥深くまで侵入し、かつ最終的に適切な配位数で結合できるため、ドーパントとして活性化されるものと考えられる。

【0031】そのため100℃といった熱的な拡散が全く期待できない低温においても、効果的なドーピングが行え、かつ高速に加速されたイオンを打ち込んだ場合のようなダメージがないために、後処理としてのアニーリングも不要になると考えられる。

【0032】また、熱CVD法やプラズマCVD法において、ドーパントを含む雰囲気中で半導体が堆積される場合と異なり、本発明の方法では半導体の母体のネットワークはドーパントの影響なしに形成されるため、形成されたp型層やn型層は優れた特性を示すことが期待できる。

【0033】さらにスパッタリング法の場合には、ドーパント原子がターゲットから試料に向かってかなりの方向性をもって飛び出すため、ガスとしてドーパントが供給される場合に比べ、不要な場所へのドーパントの拡散が大幅に減少することが期待できる。

【0034】ターゲットについて、本発明の方法を実施するにあたって用いるターゲットの材料としては所望のドーパント元素の単体を用いることができる。すなわちSiやGe等の4族半導体ではp型とするためにはB、Al、Ga、In、Tlの単体または合金を、n型とするためにはP、As、Sb、Biの単体または合金を用いればよい。これらの材料の純度は高い方がよいが、一般的には99.9%、不純物の種類によっては99%程度でも使用可能である。また、ターゲットの形状としてはプレート状のものが使い易いが、粉末状の材料をプレスしたもの、またカソードか上向きの場合にはカソードの上に粉末を盛っただけでもよい。

【0035】スパッタリングの雰囲気ガスについて、スパッタリング法では雰囲気ガスとしてArが最も一般的に用いられている。これはArがイオン化率が高く、ターゲット原子を最も効率的に打ち出すためである。しかしドーピングの目的ではあまり大きな堆積速度は必要ないことが多く、Ar以外にHe、Ne、Kr、Xe等の不活性ガスを用いることもできる。

【0036】ドーピング条件について、本発明の方法はSiやGe及びその合金またSiC等の4族の半導体ばかりでなく、GaAs、InP等の化合物半導体に対しても適用可能である。ただしドーパントは母体の半導体に応じて2族、4族、6族の元素から適宜選択する。放電の雰囲気ガスとしてAr等の不活性

8

ガスの流量は試料の大きさに応じて適宜決められる。放電時の圧力は 1×10^{-4} から0.5 Torr、好ましくは 5×10^{-4} Torrから0.1 Torrとする。放電電力も試料の大きさに応じて決められるが30cm角の試料の場合、100Wから5kW、好ましくは250Wから2kW程度とする。基板温度としては室温で良好な結果が得られる場合もあるが、一般には60℃以上とする。殆どの場合200℃程度で十分な効果が得られる。

【0037】紫外光の照射方法について、照射に用いる光としては波長150nm以上300nm以下、さらに好ましくは波長250nm以下の紫外光が効果的である。光源としては、市販の水銀灯が好適に用いられる。ただし空気中ではこのような波長領域の光は吸収を受けオゾンを発生するので、図1のドーピング装置のように光源は真空チャンバーの中に設けるのが好ましい。

【0038】図1のドーピング装置の場合には光源112、113はターゲット109の近傍に設けられているため、長時間にわたって使用すると汚れが付着して

【0039】またこの構成では大面積の試料表面全体にわたって均一に紫外光を照射するのは困難である。

【0040】しかし実験2において示したように、紫外光の照射は、ドーパントの堆積の後に行っても効果があることから、図3に示したように、大型のチャンバー301内において、光源312をカソード304から離れた位置に設け、アノード303をスパッタリングの後、光源313の位置に移動して紫外光の照射を行うようにしてもよい。

【0041】図3において、真空ポンプ302、アノード303、カソード304、試料305、ヒーター306、電源308、ターゲット309、ポンプ310、マスフローコントローラー311及びバタフライバルブ314は、それぞれ図1に示す真空ポンプ102、アノード103、カソード104、試料105、ヒーター106、電源108、ターゲット109、ポンプ110、マスフローコントローラー111及びバタフライバルブ114と実質的に同等のものが使用可能である。特に大型の装置の場合には、図3の構成の方が設計が容易である。またドーピング層を厚くしたい場合には、スパッタリングを一度にあまり長時間続けず、この移動を複数回繰り返したほうがよい。

【0042】

【実施例】以下に、本発明の半導体表面処理方法及び装置の実施例を述べて本発明をさらに説明するが、本発明はこれにより何等限定されるものではない。

【0043】実施例1

本実施例においては、図4の断面模式図に示す層構成のpin型a-Si光起電力素子408を図1に示す装置を用いて作製した。この光起電力素子408は、基板4

9

01上に下部電極402、n型半導体層403、i型半導体層404、p型半導体層405、透明電極406及び集電電極407をこの順に堆積形成した光起電力素子である。なお、本実施例の光起電力素子408では透明電極406の側より光の入射が行われることを前提としている。

【0044】まず、ステンレス製角型基板(5cm×5cm)を市販のスパッタ装置(アルバック社製、SBH-2206DE)にセットし、Ag(99.99%)をターゲットとして用いて0.3μmのAg薄膜を、また連続してZnO(99.9%)をターゲットとして用いて1.5μmのZnO薄膜をスパッタ蒸着し、下部電極402を形成した。

【0045】引き続き、この下部電極402の形成された基板を市販のプラズマCVD装置(アルバック社製、CHJ-3030)にセットした。排気ポンプにて、反応容器の排気管を介して、荒引き、高真空引き操作を行った。このとき、基板の表面温度は250℃となるよう、温度制御機構により制御した。

【0046】十分に排気が行われた時点で、ガス導入管よりSiH₄、300sccm、SiF₄、4sccm、PH₃/H₂(1% H₂希釈)55sccm、H₂、40sccmを導入し、スロットバルブの開度を調整して、反応容器の内圧を1Torrに保持し、圧力が安定したところで、直ちに高周波電源より200Wの電力を投入した。プラズマは5分間持続させた。これにより、n⁺半導体層403としてのn⁺a-Si:H:F膜が下部電極402上に形成された。

【0047】再び排気した後に、今度はガス導入管よりSiH₄、300sccm、SiF₄、4sccm、H₂、40sccmを導入し、スロットバルブの開度を調整して、反応容器の内圧を1Torrに保持し、圧力が安定したところで、直ちに高周波電源より150Wの電力を投入した。プラズマは40分間持続させた。これにより、i型半導体層404としてのa-Si:H:F膜がn型半導体層403上に形成された。

【0048】次に基板401をプラズマCVD装置より取り出し、図1に示すトーピング装置にセットした。遷移元素(E)をターゲットとして、Ar流量5sccm、圧力2×10⁻³Torr、基板温度100℃、放電電力200Wの条件で紫外光を照射しつつ70秒間放電を継続し、p型半導体層405がi型半導体層404上に形成された。

【0049】次に真空蒸着により透明電極406(ITO(In₂O₃+SnO₂))を形成し、さらに集電電極407(A1)をマスク蒸着して光起電力素子408を完成した。

【0050】作製した光起電力素子408について、エアマス(以降AMと記す)1.5(100mW/cm²)の光照射下にて特性評価を行ったところ、光電変換効

(6)

特開平5-24976

10

率(η)で9.3%が得られた。また、AM1.5(100mW/cm²)光の500時間連続照射後の光電変換効率の初期値に対する変化率を測定したところ20%以内に納まった。

【0051】実施例2

本実施例においては、図6の断面模式図に示す層構成のa-Si/a-SiタンDEM型光起電力素子613を図5に示すロールトゥロール装置542を用いて作製した。

【0052】この光起電力素子613は、基板601上に下部電極602、第1のセル611を構成するn型半導体層603、i型半導体層604、p型半導体層605、さらに第2のセル612を構成するn型半導体層606、i型半導体層607、p型半導体層608、さらに透明電極609及び集電電極610をこの順に堆積形成した光起電力素子である。なお、本実施例の光起電力素子613では透明電極609の側より光の入射が行われることを前提としている。

【0053】図5のロールトゥロール装置542は、ステンレス鋼製の帯状基板504に連続的に光起電力素子を形成するものである。同図の装置は、基板送り出し室503、第1のn型チャンバー513、第1のi型チャンバー522、第1のp型チャンバー532、第2のn型チャンバー(不図示)、第2のi型チャンバー(不図示)、第2のp型チャンバー(不図示)、及び基板巻取り室539がこの順に配置されている。第2のn型チャンバー、第2のi型チャンバー、第2のp型チャンバーは、それぞれ第1のn型チャンバー513、第1のi型チャンバー522、第1のp型チャンバー532と全く同じ構成である。各チャンバー間はガスケット507、515、524、533、536(他不図示)により隔離され、チャンバー間の不純物の侵入を防止している。

【0054】同図においてまず基板送り出し室503は、帯状基板504がセットされる室であり、成膜中はこの室からガイドローラ505を介して反応室へ基板が連続的に搬入される。また排気口502及びバルブ501を介して真空排気される。基板巻取り室539は、成膜された帯状基板538が巻取られる室であり、成膜中はこの室へガイドローラ537を介して反応室から基板が連続的に搬入される。また排気口540及びバルブ541を介して真空排気される。

【0055】n型チャンバー513及びi型チャンバー522は、プラズマCVDチャンバーであり、それぞれn型半導体層及びi型半導体層を堆積する。各チャンバー513、522内で基板は基板加熱ヒータ514、523により加熱され所定の基板温度に制御される。原料ガスは原料ガス供給管510、518より供給され、シールド板512、521により流れが整えられ、カソード511、520と基板間に生じられたプラズマにより分解され基板上に半導体膜が形成され、さらに排気口5

11

09、519より排気される。

【0056】p型チャンバー532は本発明の方法を用いた本発明のドーピング装置の実施態様である。基板は基板加熱ヒータ531により所定温度に制御される。チャンバー内は排気口528より真空排気される。カソード529の表面には遷移元素(B)のターゲット530がセットされている。このロールトゥロール装置542では基板がアノードとして機能しカソード529との間にプラズマが生起される。紫外光の光源530は、カソードの横に設けられ、基板の移動に伴いますi型半導体層の上にドーパントが堆積された後、紫外光が照射されドーパントが活性化されるようになっている。この構成により、長時間にわたる紫外光源の連続使用が可能となる。Arは原料ガス供給管527より供給される。

【0057】ガスカート507、515、524、533、536(他不図示)には、チャンバー間のガスを隔離するためにAr、酸素等の掃引ガスがガス導入口506、508、516、517、525、526、534、535(他不図示)より導入される。

【0058】このようなロールトゥロール装置542を用いて光起電力素子613を作製した。

【0059】まず、ステンレス鋼製帯状基板を連続スパッタ装置(不図示)にセットし、Al-Si(5%Si)をターゲットとして用いて0.2 μ mのAl-Si薄膜を、また連続してSnO₂(99.99%)をターゲットとして用いて0.1 μ mのSnO₂薄膜をスパッタ蒸着し、下部電極602を形成した。

【0060】引き続き、この下部電極602の形成された帯状基板を図5で示したロールトゥロール装置542にセットした。その後、排気ポンプ(不図示)にて、各チャンバーの排気管を介して真空引き操作を行った。このとき、基板の表面温度は250℃となるよう、温度制御機構により制御した。

【0061】十分に排気が行われた時点で、ガス導入管510、518より、n型チャンバーにはSiH₄/PH₃/H₂を、i型チャンバーにはSiH₄/SiF₄/H₂を、p型チャンバーガスゲートにはArガスを導入し、n型及びi型チャンバーの内圧を100mTorrにまたp型チャンバーの圧力は50mTorrに保持した。

【0062】圧力が安定したところで、各高周波電源より電力を投入し、各々のチャンバー内でプラズマを生起させ、また光源を点灯し、放電等が安定したところで帯状基板を搬送スピード20cm/minで図中左側から右側方向へ搬送させ、連続して、n、i、p、n、i、p型半導体層を積層形成した。

【0063】帯状基板の全長にわたって半導体層を積層形成した後、冷却後取り出し、ITO(In₂O₃+SnO₂)連続蒸着装置(不図示)にセットし帯状基板全長にわたって厚さ700ÅのITO層を蒸着し、透明電極

(7)

特開平5-24976

12

609とした。さらに、連続モジュール化装置(不図示)にて35cm×70cmの太陽電池モジュールを連続作製した。

【0064】作製した太陽電池モジュールについて、AM1.5(100mW/cm²)光照射下にて特性評価を行ったところ、光電変換効率(η)で8.0%以上が得られ、更にモジュール間の特性のバラツキは7%以内に納まっていた。

【0065】また、AM1.5(100mW/cm²)光の500時間連続照射後の光電変換効率の初期値に対する変化率を測定したところ16%以内に納まった。

【0066】これらのモジュールを接続して1kWの高力供給システムを作製することかできた。

【0067】比較のため、各ガスカートに掃引ガスを流さずに同様な光起電力素子を作成したところ、光電変換効率(η)7.8%以上が得られ、500時間後の劣化率は18%以内に納まっていた。すなわち掃引ガスを用いないとも各チャンバー間のドーパントの拡散の影響は若干認められるものの、軽微であった。

【0068】実施例3

本実施例においては、実施例2と同様に図6の断面模式図に示す層構成のa-Si/a-Siタンデム型光起電力素子を図5に示すロールトゥロール装置542を一部改造した装置(不図示)を用いて作製した。図5の装置と異なるのは第2のn型チャンバーに第1または第2のp型チャンバーと全の同じ本発明のドーピング装置を用いたことである。

【0069】第1及び第2のp型チャンバーには遷移元素(B)のターゲットを、また第2のn型チャンバーにはアンチモン(Sb)のターゲットを用いている。

【0070】このようなロールトゥロール装置を用いて光起電力素子613を作製した。

【0071】まず、実施例2と同様にステンレス鋼製帯状基板を連続スパッタ装置にセットし、Al-Si(5%Si)をターゲットとして用いて0.5 μ mのAl-Si薄膜を、また連続してZnO(99.99%)をターゲットとして用いて0.5 μ mのZnO薄膜をスパッタ蒸着し、下部電極602を形成した。

【0072】引き続き、この下部電極602の形成された帯状基板を本実施例のロールトゥロール装置にセットした。その後、排気ポンプにて、各チャンバーの排気管を介して真空引き操作を行った。このとき、基板の表面温度は250℃となるよう、温度制御機構により制御した。

【0073】十分に排気が行われた時点で、ガス導入管より、第1のn型チャンバーにはSiH₄/PH₃/H₂を、第1及び第2のi型チャンバーにはSiH₄/SiF₄/H₂を、第1、第2のp型チャンバー及び第2のn型チャンバーガスゲートにはArガスを導入し、スロットバルブの開度を調整して、第1のn型及び第

13

1. 第2のi型チャンバーの内圧を100mTorrに、また第2のn型チャンバー及び第1、第2のp型チャンバーの圧力は50mTorrに保持した。圧力が安定したところで、各p型チャンバーの光源を点灯し、各高周波電源より電力を投入し各々のチャンバー内でプラズマを生起させ、放電等が安定したところで帯状基板を搬送スピード20cm/minで搬送させ、連続して、n、i、p、n、i、p型半導体層を積層形成した。

【0074】帯状基板の全長にわたって半導体層を積層形成した後、冷却後取り出し、さらにITO(In₂O₃+SnO₂)層を蒸着して透明電極609を形成し、連続モジュール化装置にて30cm×120cmの太陽電池モジュールを連続作製した。作製した太陽電池モジュールについて、AM1.5(100mW/cm²)光照射下にて特性評価を行ったところ、光電変換効率(η)で8.5%以上が得られ、さらにモジュール間の特性のバラツキは10%以内に納まっていた。

【0075】また、AM1.5(100mW/cm²)光の500時間連続照射後の光電変換効率の初期値に対する変化率を測定したところ15%以内に納まった。

【0076】実施例4

本実施例においては、図7の断面模式図に示す層構成のa-SiC/a-Si/a-SiGeトリプル型光起電力素子を図5に示すロールトゥロール装置542を一部改造した装置(不図示)を用いて作製した。本実施例で用いた装置は、実施例2で用いた装置にさらに第3のn型i型及びp型チャンバーを追加したものであり、第1から第3のp型チャンバーのみが本発明のドーピングチャンバー、他のチャンバーはプラズマCVDチャンバーである。

【0077】このようなロールトゥロール装置を用いて図7に示す光起電力素子717を作製した。

【0078】この光起電力素子717は、基板701上に下部電極702、第1のセル714を構成するn型半導体層703、i型半導体層704、p型半導体層705、さらに第2のセル715を構成するn型半導体層706、i型半導体層707、p型半導体層708、さらに第3のセル716を構成するn型半導体層709、i型半導体層710、p型半導体層711、さらに透明電極712及び集電電極713をこの順に堆積形成した光起電力素子である。なお、本実施例の光起電力素子717では透明電極712の側より光の入射が行われることを前提としている。

【0079】まず、実施例2と同様にステンレス製帯状基板を連続スパッタ装置にセットし、Al(99.9%)をターゲットとして用いて0.3μmのAl薄膜を、また連続してZnO(99.99%)をターゲットとして用いて0.3μmのZnO薄膜をスパッタ蒸着し、下部電極702を形成した。

【0080】引き続き、該下部電極702の形成された

(8)

特開平5-24976

14

帯状基板をロールトゥロール装置にセットした。その後、排気ポンプにて、各チャンバーの排気管を介して真空引き操作を行った。このとき、基板の表面温度は250℃となるよう、温度制御機構により制御した。

【0081】十分に排気が行われた時点で、ガス導入管より、各n型チャンバーにはSiH₄、PH₃、B₂H₆を、第1のi型チャンバーにはSiH₄、GeH₄、B₂H₆を、第2のi型チャンバーにはSiH₄、SnF₄、B₂H₆を、第3のi型チャンバーにはSiH₄、GeH₄、B₂H₆を、また各p型チャンバー、ガスゲートにはArガスを導入し、スロットルバルブの開度を調整して、各n型及び各i型チャンバーの内圧を100mTorrに、また各p型チャンバーの圧力は50mTorrに保持した。

【0082】圧力が安定したところで、各p型チャンバーの光源を点灯し、各高周波電源より電力を投入し各々のチャンバー内でプラズマを生起させ、放電が安定したところで帯状基板を搬送スピード30cm/minで搬送させ、連続して、n、i、p、n、i、p型半導体層を積層形成した。

【0083】帯状基板の全長にわたって半導体層を積層形成した後、冷却後取り出し、さらにITO(In₂O₃+SnO₂)層を蒸着して透明電極609を形成し、さらに連続モジュール化装置にて30cm×120cmの太陽電池モジュールを連続作製した。

【0084】作製した太陽電池モジュールについて、AM1.5(100mW/cm²)光照射下にて特性評価を行ったところ、光電変換効率(η)で10.2%以上が得られ、さらにモジュール間の特性のバラツキは5%以内に納まっていた。

【0085】また、AM1.5(100mW/cm²)光の500時間連続照射後の光電変換効率の初期値に対する変化率を測定したところ8%以内に納まった。

【0086】これらのモジュールを接続して5kWの電力供給システムを作製することができた。

【0087】実施例5

本実施例において図8に示すような構成の多結晶Si太陽電池801について説明する。Wacker社製の表面が研磨された直径6インチのn型多結晶Siウェハー(比抵抗2ohm-cm)を基板として用意した。弗酸にて自然酸化膜を除去した後、この基板を図1のドーピング装置と同様な構造だが大型のドーピング装置に研磨面が表向きとなるようセットした。ターゲット109として純度99.9%のGaのプレートを用いた。ドーピング条件としては、Ar流量20sccm、圧力10⁻¹Torr、基板温度100℃、放電電力は1kWとし、紫外光の照射、放電を150秒継続しp型領域802を形成した。次いでターゲット109を純度99.9%のSbのプレートに交換し、基板を裏返しにセットしなおした以外は同様のドーピング条件でn型領域803を形成し

50

た。このn⁺型領域803はいわゆるバックサーフェスフィールドを形成しキャリアの高極近傍での再結合を防ぎ、さらにオーミック性を向上させるためのものである。次に、両面にTi、Pd、Agの積層からなる集電電極804、下部電極805を電子ビーム蒸着法で形成した。表面の電極は光の入射をあまり妨げないようにマスクをかけてグリット状とした。電極を形成した後400℃にて2分間シタリングを行った。次いで表面にZnSとMgF₂を積層し反射防止層806とした。

【0088】この試料を2cm角に切って太陽電池特性を評価したところ、光電変換効率(η)が15.24±0.61%と極めて優れた特性及び均一性が得られた。

【0089】実施例6

本実施例は図9にその断面構造を示すa-Si₁薄層トランジスタ(TFT)の例である。コーニング#7059ガラスを基板901としてこの上にCrを蒸着し、さらにフォトリソグラフィ工程にてゲート902を形成した。次いで市販の容量結合型高周波グロー放電装置にてSiH₄とアンモニア(NH₃)を原料ガスとして厚さ3000Åのアモルファス窒化シリコン(a-Si₃N₄)層903を堆積した。この上に同じ装置を用いて厚さ2000Åの1型a-Si₁層904を堆積した。この上に同じ装置で再び厚さ3000Åのa-Si₁N層を堆積しチャネル905を残してフォトリソグラフィ工程にてエッチングした。この後試料を実施例5で用いたものと同等のドーピング装置にセットしターゲットとして純度99%のPのプレートを用い、ドーピング条件としてArの流量30sccm、圧力5×10⁻¹Torr、基板温度80℃、放電電力800Wとして紫外光の照射、放電を200秒間継続しn⁺型領域906を形成した。ここでチャネル905のa-Si₁Nは絶縁体であるため表面にドーピングによる低抵抗領域ができることはない。次いでこの上にAlを厚さ2000Å蒸着し、さらにチャネル905をフォトリソグラフィ工程にてエッチングしソース907、ドレイン908としてTFTを形成した。なおここでチャネル長は10μmである。このようにして製造されたTFTのゲート902、ソース907、ドレイン908に各々導線を固着しトランジスタ特性を20cm角の範囲にわたって評価した。ドレイン電圧15Vのとき、ゲート電圧15Vと0VとのON/OFF比は1.5×10³倍±8%と優れたものであった。本発明の方法ではチャネル部がa-Si₁Nで保護されエッチング等の処理を受けないためON/OFF比が大きかつ均一性も優れていると考えられる。したがって本発明の方法によるTFTは大型の液晶ディスプレイのアクティブマトリクス回路に用いるのに最善なものである。

【0090】

【発明の効果】本発明のドーピング方法及び装置によれば、良質な半導体の母体に対して大きな損傷を与えずにドーピングが行え、かつ高温での後処理が不要なため単結晶、多結晶、アモルファスであるを問わず、各種の半導体に対して、特性の優れたp型またはn型の半導体領域を形成することができ、しかもドーパントの不要な拡散がないため特性の優れた半導体デバイスを得ることができる。また装置の構成が簡単であり、大面積にわたって均一な特性が得られ、処理時間が短いため、特に大型の太陽電池や液晶ディスプレイのアクティブマトリクス回路等を低コストにて製造することができる。

【図面の簡単な説明】

【図1】本発明のドーピング方法を実施するのに好適な本発明のドーピング装置の実施態様を示す概略構成図である。

【図2】本発明のドーピング方法で作成したa-Si₁太陽電池を示す断面模式図である。

【図3】本発明のドーピング方法を実施するのに好適な本発明のドーピング装置の別の実施態様を示す概略構成図である。

【図4】本発明のドーピング方法で作成したシングル型a-Si₁太陽電池を示す断面模式図である。

【図5】本発明のドーピング装置を組み込んだロールトゥロール装置の一例を示す概略構成図である。

【図6】本発明のドーピング方法で作成したタンデム型a-Si₁太陽電池を示す断面模式図である。

【図7】本発明のドーピング方法で作成したトリプル型a-Si₁太陽電池を示す断面模式図である。

【図8】本発明のドーピング方法で作成した多結晶Si太陽電池を示す断面模式図である。

【図9】本発明のドーピング方法で作成したa-Si₁TFTを示す断面模式図である。

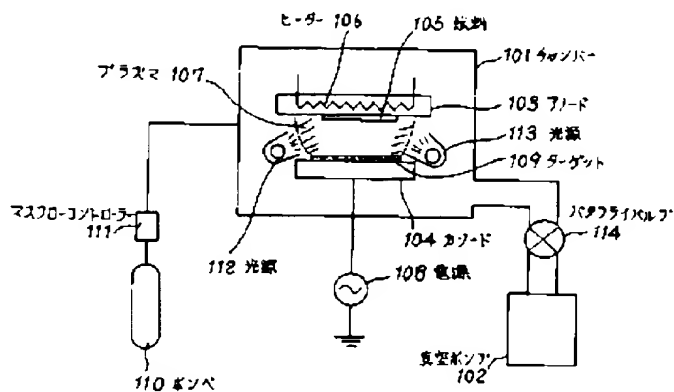
【符号の説明】

- | | |
|----------|--------------|
| 101 | チャンバー |
| 102 | 真空ポンプ |
| 103 | アポート |
| 104 | カソード |
| 105 | 試料 |
| 106 | ヒーター |
| 107 | プラズマ |
| 108 | 電源 |
| 109 | ターゲット |
| 110 | ボンベ |
| 111 | マスフローコントローラー |
| 112, 113 | 光検 |

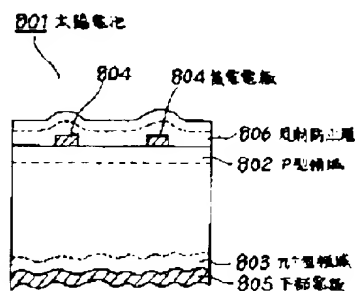
(10)

特開平5-24976

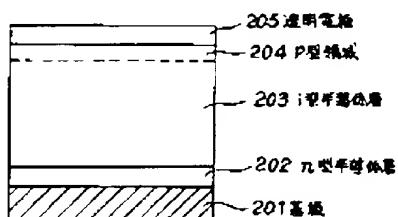
【図1】



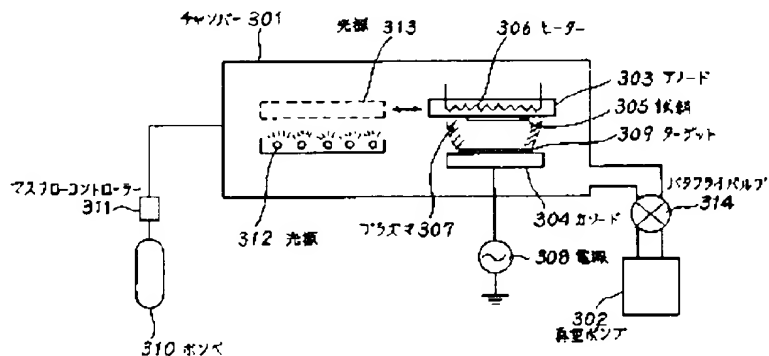
【図8】



【図2】



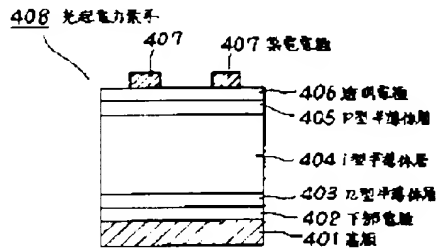
【図3】



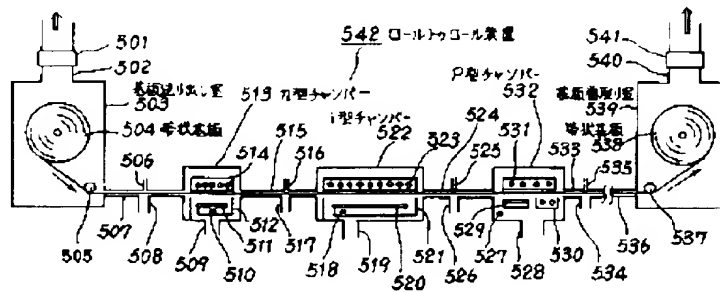
(11)

特開平5-24976

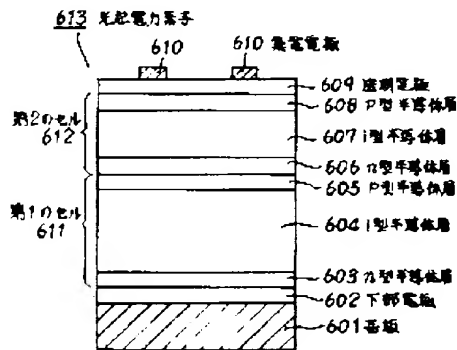
【図4】



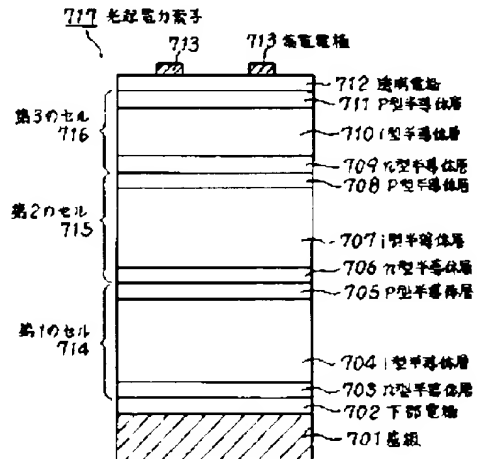
【図5】



【図6】



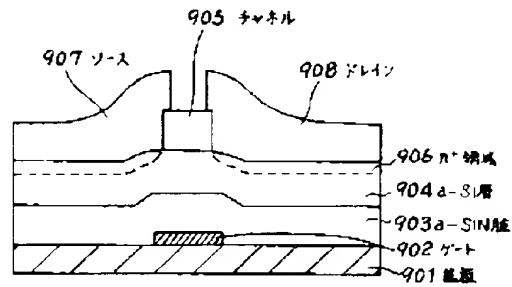
【図7】



(11)

特開平5-24976

【図9】



フロントページの続き

(51)Int.Cl.³

H01L 29/784
31/04

識別記号

庁内整理番号

F I

技術表示箇所

Searching by Document Number

** Result [Patent] ** Format [P-03] 17-Apr-2013

Application no/date: 1991-186489[1991/07/25]
 Date of request for examination: []
 Public disclosure no/date: 1993- 24976[1993/02/02] **¥ Translate**
 Examined publication no/date [old law]: []
 Registration no/date: []
 Examined publication date (present law): []
 PCT application no: []
 PCT publication no/date: []
 Applicant: CANON INC
 Inventor: NAKAGAWA KATSUMI, TAKABAYASHI MEIJI, TAKEUCHI EIJI
 IPC: C30B 29/06 C30B 31/20 H01L 21/22
 H01L 29/784 H01L 31/04
 FI: C30B 29/06 C30B 31/20 H01L 21/22 E
 H01L 29/78 , 311F H01L 31/34 B H01L 29/78 , G16L
 F-term: C121FA02, FA04, FA06, FA13, FA14, FA15, FA18, GA02, GA11, HA03, AA01, AA03,
 AA05, AA08, AA16, BA14, CA07, CA08, CA16, CA34, CA35, CA36, CA37, CB14, CB15, CB18, CB21,
 CB27, CB34, CB39, DA04, DA16, DA17, DA20, FA01, 4G077AAC3, BA14, BE31, BE41, DA11, EA06,
 EB05, EG22, EG23, EJ04, HA06, 3F111NN16, NN24, NN35, QQ11, AA09, AA16, AA17, AA26, AA28,
 BB01, CC09, CC11, BE04, EE13, FF03, FF07, GG12, GG15, GG24, GG25, GG32, GG42, HJ01, HJ16,
 HJ23, HK17, HK32, NN14, NN15
 Expanded classification: 1-1, 301, 422, 440
 Fixed keyword: B, C4, E, 11
 Citation:
 Title of invention: METHOD FOR DOPING SEMICONDUCTORS AND APPARATUS THEREFOR
 Abstract:

PURPOSE: To provide a doping apparatus capable of obtaining a p type or n type semiconductor having excellent properties, capable of obtaining properties uniform over a large area and capable of manufacturing a large sized semiconductor device at a low cost.

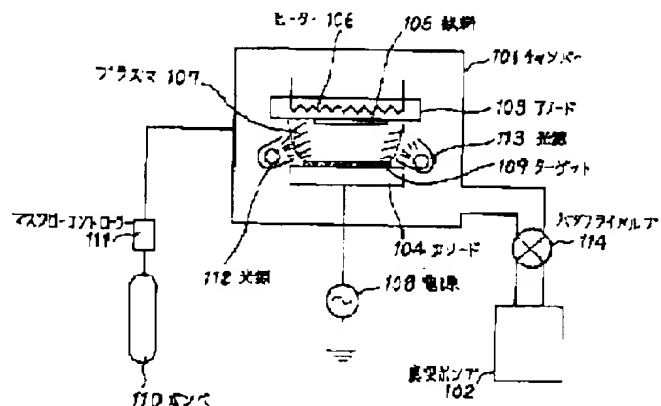
CONSTITUTION: The inside of a chamber 101 is provided with a pair of electrodes, i.e., an anode 103 and a cathode 104. The anode 103 is set with a sample 105. The sample 105 can be heated by a heater 106. The cathode 104 is connected to a power source 108 for generating a plasma 107 between the anode 103 and the cathode 104. A target 109 is set on the cathode 104. An inert gas is introduced into the chamber 101 from a cylinder 110. Furthermore, the inside of the chamber 101 is provided with light sources 112 and 113 of ultraviolet light as well, and irradiation on the surface of the sample 105 is permitted as occasion demands.

COPYRIGHT: (C)1993, JPO&Japio

3/13/02

LI ANSWER 3 OF 4 HCAPLUS COPYRIGHT 2002 ACS
AN 1994:42612 HCAPLUS
DN 120:42612
TI Doping of semiconductor and apparatus therefor
IN Nakagawa, Katsumi; Takabayashi, Meiji; Takeuchi, Eiichi
PA Canon Kk, Japan
SO Jpn. Kokai Tokkyo Koho, 12 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
ID ICM C30B025-06
ICS C30B031-20; H01L021-22; H01L029-784; H01L031-04
CC 75-12 Crystallography and Liquid Crystals)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	JP 05024976	A2	19930202	JP 1991-186489	19910725 <--
AB	The title method comprises irradiation of the surface of a semiconductor by UV light of 300 nm in wavelength during or after sputtering deposition of a dopant.				
ST	semiconductor doping sputtering deposition UV irradiation				
IT	Sputtering				



Priority country/date/number: () { } ()
 Classification of examiners decision/date: () { }
 Final examinational transaction/date: (withdrawal by no request for examination)
 Examination intermediate record:
 (A63 1991/ 7/25, PATENT APPLICATION UTILITY MODEL REGISTRATION APPLICATION, 1400
 (A961 1992/ 7/30, CORRECTION DATA BY EX OFFICIO (FORMALITY),
 (A300 1998/10/ 8, MAKING OF FILE WRAPPER EXTRACTION LIST OF UNREQUEST FOR EXAMIN

*** Trial no/date [] Kind of trial [] ***
 Demandant: -
 Defendand: -
 Opponent: -
 Classification of trial decision of opposition/date: () { }

Final disposition of trial or appeal date: []

Trial and opposition intermediate record:

Registration intermediate record:

Amount of annuities payment: [] year

Lapse date of right: []

Proprietor: []

Other Drawings...

(57)

[ABSTRACT]

[CONSTITUTION]

Anode 103 and cathode 104-1 bigeminal electrode is installed in chamber 101. Sample 105 is set to anode 103. Sample 105 can heat by means of heater 106. As for cathode 104, it is connected plasma 107 to occurrence power source 108 to do between anode 103, cathode 104. Target 109 is set on cathode 104. Inert gas is introduced into chamber 101 from bomb 110. In addition, Light source 112,113 of ultraviolet radiation more are installed in chamber 101, and face of sample 105 gets possible to be irradiated at any time.

[EFFECT]

Semiconductor of superior p type or n mold of character can be got, audacious behavior product is lasted for, and the characteristic which is uniformity is provided, large-scale semiconductor devices can be produced in cost low.

[WHAT IS CLAIMED IS:]

[Claim 1]

While, by means of target containing a *dopanto* element, making *dopanto* accumulate in the surface of semiconductor by sputtering method, at a minimum, ultraviolet radiation including constituent of less than or equal to wave length 300nm is triggered in the surface of above semiconductor, and it is doping method of semiconductor doing doping in above semiconductor.

[Claim 2]

After, by means of the target which contained a *dopanto* element, having accumulated in said face in *dopanto* by sputtering method, at a minimum, ultraviolet radiation including constituent of less than or equal to wave length 300nm is triggered in said surface, and it is doping method of semiconductor doing doping in above semiconductor.

[Claim 3]

Doping apparatus of the semiconductor which comprised line for, at a minimum, the target which contained *dopanto* chemical element in anode and surface installed in internal of the chamber that the evacuation that semiconductor was set was possible and above chamber to supply inert gas in the light source which, at a minimum, irradiated ultraviolet radiation including constituent of less than or equal to wave length 300nm in the surface of the power source which supplied electric power in set cathode and said cathode and above semiconductor and above chamber.

[Claim 4]

Doping apparatus of semiconductor as claimed in claim 3 comprising measure transporting semiconductor between location opposed to light source irradiating lay opposed to target and ultraviolet radiation.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[INDUSTRIAL APPLICATION FIELD]

The present invention relates to doping method of the semiconductor which is optimum in quantity production of audacious behavior product semiconductor devices of active matrix circuit of a liquid crystal display of the solar cell which is high efficiency and doping apparatus.

[0002]

[PRIOR ART]

There is direction of audacious behavior *sekika* represented along with *bisaika* represented as current of recent semiconductor devices art by semiconductor memory and an image sensor, direction of integration by solar battery and active matrix circuit of a liquid crystal display. In audacious behavior product semiconductor devices, it is had to move manufacture cost per a unit area as much as possible.

Therefore semiconductor film of amorphous and polycrystal accumulated on inexpensive basal plate such as glass, metal, ceramics begins to be used along with a single crystal silicon wafer as semiconductive material. However, *kosutoka* is called for about each other manufacture process low to move manufacture cost of a device. In addition, A produced device lasts for 30cm angle or audacious behavior product more than it, and characteristic must be uniformity. In other words, The process technology which is good for it must be developed to an audacious behavior product device.

[0003]

Doping technology is given as the most important art in terms of audacious behavior *sekika* in each manufacture process.

[0004]

It is thermal diffusion method that have been most generally used as doping art of semiconductor. Thermal diffusion method is technology conventional 1000 degrees Celsius scatter dopant atom included in semiconductor face in swabbing or accumulated membrane within semiconductor in high temperature older than, and to activate as *dopanto*. This method can apply to an audacious behavior product device comparatively easily, but, if film semiconductor is used to use high temperature, it saishi, and it has limitaion in basal plate available. In addition, It is needed for processing for a long time (for conventional around several hours), and through-put of manufacture is not preferable.

[0005]

In addition, There is ion implantation method as other generic doping art. In this approach, After having removed impurity from beam of the dopant atom ion which ionized in vacuum by measure of mass analysis, it is the method which it accelerates in electric field, and ramming down, conventional 800 degrees Celsius are annealed in temperature older than within semiconductor for around several hours, and activate *dopanto*. In this approach, Control of *dopanto* is easy to do, but, it is necessary to scan beam over audacious behavior product, and through-put of also manufacture is not preferable. In addition, Large-scaled, apparatus becomes disadvantageous on also cost side.

[0006]

On the other hand, There is method gas including *dopanto* is mixed within vapor phase in pile of film in the event of film semiconductor to accumulate from gas phase in method such as thermal CVD or plasma CVD, and to introduce dopant atom into within film semiconductor. In this approach, Audacious behavior *sekika* is comparatively preferable when through-put is compared with thermal diffusion method and ion implantation method in easy, but, it was tended characteristic of semiconductor of formed n pattern or p pattern was not always enough, and to be imperfection in application to semiconductor devices. When, for well-known example, it accumulates in polycrystal Si by thermal CVD, when phosphine (P H_3) is mixed in mono-silane of charge stock (Si H_4), and it is going to be done in n pattern, crystal grain of Si becomes particularly small in high concentration, and characteristic as n pattern Si does in n pattern by thermal diffusion method and *ioninpuratesyon* method, it is to the thing which it is compared and was inferior to. In addition, When it accumulates in amorphous silicon (a-Si) by plasma CVD method, when diborane ($\text{B}_2 \text{H}_6$) is mixed to Si H_4 of charge stock, and it is going to be done in p pattern, band gap of optics (E_g) falls, it is to the thing which localization level increases, and the characteristic as p pattern semiconductor was inferior to.

[0007]

When gas including *dopanto* is mixed within gas phase for the reason, reaction of gas including chemical element of basis composing semiconductor (Si) is had an influence on, when a pre-cursor of pile of semiconductor (accretion reactive precursor) is changed, it is conceivable.

[0008]

In addition, When doping is done by accretion, specific locality in basal plate cannot form semiconductor regions of n pattern and p pattern for selection to the public. Because of this process becomes complicated in application to a liquid crystal display in particular. Some proposal does from such a point of view.

[0009]

M.B. It is N Spitzer and S. Bunker does phosphorous (P) ion implantation without doing mass analysis in p type single crystal Si, solar battery of conversion efficiency 15% to have p-n junction was made (16th IEEE Photovoltaic Conf.) SanDiego, 1982p.711-) B (Proc.3rd PVSEC in Japan ('82) p.7-) that H.Itoh made solar cell of conversion efficiency 10% with similar method without an anti-reflective layer B It becomes comparatively easy, and, by *ioninpuratesyon* method which does not do mass analysis, apparatus improves through-put of manufacture. However, aftertreatment of the audacious behavior product which is enough in application to solar cell is distress. In addition, After having driven ion in

their experiment, annealing is done in 550 degrees Celsius or more than 600 degrees Celsius, through-put of manufacture is low, and there is much constraint as against application to film semiconductor.

[0010]

In addition, S.D. Westbrook disassembles gas including boron (B) in glow discharge, even more particularly, it accelerates in boron ion by applying electric field, after having driven into n pattern monocrystal Si, 550 degrees Celsius are older than, and it is annealed, and it is (Appl. making solar battery of conversion efficiency 19% Phys. Lett. Vol. 50 ('87) p.469-) B On the other hand, Yoshida, setsune, Hirao do doping to a-Si of Lin by means of similar apparatus, and film transistor (TFT) is made (IEEE Elec.) Device Lett. Vol. 9 (1988) p.90-) B Audacious behavior *sekika* is easy to be held in these method, through-put of manufacture is comparatively preferable, too. In addition, Locality of specify of semiconductor side can form domain of p pattern or n pattern for selection so that it is shown in the latter. However, various unnecessary ion is driven in high speed aside from *dopantoion* not to do mass analysis. Therefore, Damage by ion in particular is hard to be removed in enough temperature in the event of a-Si that it is difficult that it is annealed, that application to a-Si solar battery is hit, it obstructed. In addition, Control cannot be done about neutral dopant atom aside from ion, these dopant atom is easy to be scattered in each part of apparatus. Conventional pin inosulation is used in particular in a-Si solar cell, at a minimum, it is from six levels, nine levels in n pattern, i pattern, the tandem a-Si cell which, even more particularly, laminated pin conjugation of a plural number from three levels of p pattern. When foreign semiconductor layer of adjacent *do* electroforming (i layer in particular) is contaminated with these *dopanto*, adverse effect is easy to be given characteristic of a device. Above all, diffusion of *dopanto* to chamber to layer which it is directed to mass production of a-Si solar cell, and is next to cingulate basal plate of lengthiness of a reel of film or tape in the roll two roll apparatus which continuation accumulates is easy to be had.

[0011]

As thus described it was necessary to improve doping art to audacious behavior product more to mass-produce the a-Si solar cell which was high efficiency. In addition, Development of preferable doping technology of through-put of manufacture was expected in the case of crystalline semiconductor solar cell and liquid crystal display.

[0012]

[PROBLEM TO BE SOLVED BY THE INVENTION]

The present invention is the thing which took warning by such an actual condition, and, in manufacture of semiconductor devices, apparatus for unnecessary diffusion to carry out the method which audacious behavior product is lasted for, and produce semiconductor of superior p pattern of characteristic or n pattern in the treatment time which well has a short homogeneity in a little apparatus that it is easy and this method of *dopanto* is provided, manufacture in low cost of semiconductor devices of the solar battery which is high efficiency particularly and audacious behavior product such as for example a liquid crystal display is enabled, it is directed to that the spread of these devices is contributed to.

[0013]

[MEANS TO SOLVE THE PROBLEM]

When the present invention accumulates with a dopant layer by sputtering method in the surface of semiconductor, ultraviolet radiation is irradiated in the surface of semiconductor and is as a purpose in forming domain of semiconductor of good p pattern of characteristic or n pattern by means of activating *dopanto* in the function.

[0014]

In other words, While doping method of semiconductor of the present invention uses target containing a *dopanto* element, and making *dopanto* accumulate in the surface of semiconductor by sputtering method, at a minimum, ultraviolet radiation including constituent of less than or equal to wave length 300nm is triggered in the surface of the semiconductor, and doping is done in the semiconductor.

[0015]

In addition, After doping method of semiconductor of the present invention used the target which contained a *dopanto* element, and having accumulated in the surface in *dopanto* by sputtering method, at a minimum, ultraviolet radiation including constituent of less than or equal to wave length 300nm is triggered in the surface, and doping is done in the semiconductor.

[0016]

On the other hand, Doping apparatus of semiconductor of the present invention comprises the chamber which is possible the evacuation that semiconductor is set, anode installed in internal of the chamber, the cathode that target containing *dopanto* chemical element is set by surface, power source supplying electric power in the cathode, the light source which, at a minimum, irradiate ultraviolet radiation including constituent of less than or equal to wave length 300nm in the surface of the semiconductor, and line, at a minimum, to supply inert gas in the chamber.

[0017]

Even more particularly, Doping apparatus of semiconductor of the present invention can do with a thing comprising measure transporting semiconductor between location opposed to light source irradiating lay opposed to target and ultraviolet radiation.

[0018]

[OPERATION]

FIG. 1 is outline block diagram to show embodiment of terrible - *pingu* apparatus of the preferred present invention in to carry out terrible - *pingu* method of the present invention.

[0019]

Anode 103 and electric pole of cathode 104-1 pair is installed in chamber 101 which is possible evacuation by means of vacuum pump 102. Sample 105 is set to anode 103.

[0020]

Semiconductor film of polycrystal and amorphous accumulated on basal plate such as a semiconductor wafer of single crystal and polycrystal, glass or metal for sample is used. As for these semiconductor, doping may be considered to be depending on purpose beforehand, and it needs not to be done doping. Desired temperature can heat sample 105 by means of heater 106. As for cathode 104, it is connected plasma 107 to occurrence power source 108 to do between anode 103, cathode 104. Target 109 is set on cathode 104. B, Al, Ga, In, Tl, P, As, Sb, Bi are used for material of target. Even direct-current power source is preferable for power source 108, but, even a high frequency source is preferable. When target material in particular is high drag, power source of radio frequency of 13.56MHz, for example, can employ in optimum. Inert gas of Ar is introduced into chamber 101 from bomb 110. Discharge of inert gas is adjusted by means of mass flow controller 111. And pressure in chamber 101 is adjusted by mass flow controller 111 and valve lift of butterfly valve 114. In addition, Mercury lamp 112,113 (it is written down with light source 112,113) are installed as light source of ultraviolet radiation more in chamber 101, and surface of sample 105 gets possible to be irradiated at any time.

[0021]

In confirmation of one experiment effect of the invention, it was saved, and the following experiment was done. A Si wafer of p type which sintering ring made gold electrode in rear (resistivity 1ohm / cm) was set in sample 105 and doping apparatus of *shi* FIG. 1. After having exhausted chamber 101 10 to 10^{-6} Torr once, 5sccm carries away Ar, pressure 10 was assumed 10^{-3} Torr in coordination with butterfly valve 114. Subsequently, Current of heater 106 was adjusted so that basal plate temperature became 100 degrees Celsius. Plate of elementary substance of P of fineness 99.9% was used for target 109. Subsequently, Light source 112,113 were illuminated. In this state, while, from power source 108, adjusting a matching network of non-graphic display so that echo electric power becomes very small, plasma 107 can leave occurrence when a rf power of 200W is supplied. In this state, it passed for 100 seconds, and power source 108, light source 112,113 and feed of electric power to heater 106 were left. After sample cooled off, it was taken out from chamber 101, and it was cut and brought down in 1cm angle, and it was done with sample 1A.

[0022]

Next, For comparison purposes, the other which did not illuminate light source 112,113 made one sample B with operation completely the same as the above.

[0023]

Next, Conductor was adhered in silver paste on sample 1A, rear of one B and appearance. At first, Volt-ampere characteristic in in the dark of both sample was measured. Rectification ratio 3×10^4 in 1V were ^{four} time at sample 1A. The rectification ratio got only 50 times in one sample B for it. Even more particularly, solar cell character of both sample with *sorashimyureta* of air trout (AM) 1.5 was watched. The character that conversion efficiency (eta) was good as 9.3% and solar cell without coating was provided at sample 1A. On the other hand, Conversion efficiency (eta) was inadequate for 2.7% and the function as solar cell in one sample B.

[0024]

After having sputtered in method same as experiment 1 except that light source 112,113 were not illuminated in two experiment FIG. 1, light source 112,113 are illuminated for 10 minutes. sample 2A were made. In addition, Light source 112,113 are not illuminated, and it sputters for 50 seconds. subsequently *o* irradiates ultraviolet radiation for five minutes. sputtering and ultraviolet irradiation were repeated, and two sample B was made with the same condition again.

[0025]

The rectification ratio at 1V of in the dark was 1×10^{-5} time in 2×10^3 time. two sample B at sample 2A. In addition, 7.8%, conversion efficiency of two sample B (η) were 8.5% conversion efficiency of sample 2A (η) solar cell character in AM1.5.

[0026]

Solar cell as shown in FIG. 2 was made to show that three experiment invention was effective for amorphous semiconductor. Basal plate 201 of stainless of thickness 1mm is set in commercial high frequency capacity bond type glow discharge device, subsequently n pattern semiconductor layer 202 of a Si accumulated on this top with i pattern semiconductor layer 203 of a Si. Construction condition of n type semiconductor layer 202 does SiH_4 which mixed PH_3 of 5% as charge stock gas with 5sccm, pressure 0.5Torr, discharge electric power 50W, basal plate temperature 250 degrees Celsius, film thickness is 200A. Construction condition of i type semiconductor layer 203 does SiH_4 with 20sccm, pressure 0.5Torr, discharge electric power 100W, basal plate temperature 250 degrees Celsius as charge stock gas, film thickness is 4000A. Do it this way. Sample was set in apparatus of FIG. 1. Plate of elementary substance of B of fineness 99.9% was used for target 109.

[0027]

It is done with Ar5sccm, ten pressure $^{-3s}$ Torr, basal plate temperature 200 degrees Celsius, discharge electric power 200W for doping condition, while illuminating light source 112,113, discharge was continued for 50 seconds, and p pattern domain 204 was made.

[0028]

After sample cooled off, it is taken out from chamber 101, and it sets in commercial resistance heating type metallizing apparatus, and alloy of In and Sn is deposited in oxygen atmosphere, thickness 700A accumulated, and transference electrode 205 of IT O ($\text{In} < \text{S U B} > < / \text{S U B} > \text{O}_3 + \text{SnO}_2$) layer was done with sample 3A. The sample which assumed n type semiconductor layer 202 p type a-Si bed of caliper 200A in FIG. 2 is set in doping apparatus of FIG. 1, target of P is used. P type tank 204 was formed in doping condition same as the above. In a like manner, transference electrode 205 was formed, and it was assumed three sample B.

[0029]

Both sample 3A, three B were evaluated in method same as experiment 1. Five time, three sample B 8×10 were four time sample 3A 1×10 rectification ratio at 1V. In addition, 8.5%, three sample B were 7.8%, and sample 3A showed superior characteristic in the conversion efficiency as solar cell (η) both.

[0030]

The above-mentioned experimental result is based on about mechanism of doping, and it can be supposed about mechanism of doping method of the present invention as follows. In sputtering method, there is ion of Ar within plasma of discharge, but, as for these ion, bias swats target 109 in done cathode 104 to minus number. As a result, a constituent atom of target doing recoil accumulates on sample 105. Because is not accelerated in dopant atom being neutral by electric field, in general terms, it will be hard to be invaded to the inside of sample. However, when ultraviolet radiation is irradiated by sample side, to loosen bond of atom mutual of Si composing semiconductor by energy of photon of ultraviolet radiation, atom of *dopanto*, of sample, it is deep, it is just, it is conceivable to be able to couple in appropriate coordination number penetration is done and and it is definitive when is activated as *dopanto*.

[0031]

Therefore because there is not the damage that is carbuncle when ion doping of effect do in the cryogenic temperature which thermal diffusion such as for example 100 degrees Celsius cannot quite expect and is accelerated by high speed was driven, it is thought that annealing as aftertreatment becomes needless.

[0032]

In addition, When, in thermal CVD method and plasma CVD method, is accumulated semiconductor in atmosphere including *dopanto*, that formed p pattern layer and n pattern layer show superior characteristic can be expected so that it is different, and network of ground material of semiconductor is

formed without adverse effect of *dopanto* in method of the present invention.

[0033]

When, in the event of sputtering method more, *dopanto* is supplied as gas dopant atom by target sample is gone to, and considerable polarity is had, and to begin to jump, it is compared, that diffusion of *dopanto* to unnecessary locality largely decreases can be expected.

[0034]

When method of the present invention is carried out about target, simple substance of desired *dopanto* chemical element can be used for material of target to use. In other words, If P, As, Sb, simple substance of Bi or alloy is used to do B, Al, Ga, In, simple substance of Tl or alloy with n pattern to do with p type in 4 group semiconductor such as Si or Ge, it is preferable. Purity of these material had better be high, but, even around 99% are generally available by 99.9%, class of impurity. In addition, A plate-shaped thing is easy to be used for configuration of target, but, the thing which pressed material of pulverulent and cathode served powder on cathode in the event of an upswing and are preferable.

[0035]

Ar is used for general as atmosphere gas by sputtering method about atmosphere gas of sputtering most. This is so that the factor which Ar ionizes proposes target atom for efficiency most highly. However, it is tended to be needless for much big accretion velocity in purpose of doping, and inert gas such as He, Ne, Kr, Xe can be used aside from Ar.

[0036]

Method of the present invention can be applied to for compound semiconductors such as Ga As, In P as well as semiconductor of four family such as Si and Ge and the alloy and Si C about doping condition. But, *dopanto* chooses among 2 group, 4 group, chemical element of six family depending on maternal semiconductor appropriately. Discharge of inert gas of Ar accepts size of sample as gas of atmosphere of discharge, and it is decided appropriately. 0.5Torr is preferable, and pressure 1×10 in discharge assume 0.1Torr from 5×10^{-4} s Torr from $^{-4}$. Discharge electric power is decided depending on bulk of sample, too, but, preferably, for the case sample of 30cm angle, 5kW are done with around 2kW from 250W from 100W. When good result is provided in room temperature for basal plate temperature, there is, but, it is done more than 60 degrees Celsius in general. Enough effect is provided at around 200 degrees Celsius for the case most.

[0037]

Even more particularly, preferably ultraviolet radiation of less than or equal to wave length 250nm is effective lower than 300nm more than wave length 150nm for glow to use in irradiation about irradiation method of ultraviolet radiation. For light source, commercial mercury lamp is used by optimum. But, It is desirable that glow of such a wave length territory receives absorption in the air, and light source establishes ozone in a vacuum chamber like doping apparatus of FIG. 1 in what occur.

[0038]

Fouling bonds so that light source 112,113 comprise to the vicinities of target 109 in the event of doping apparatus of FIG. 1 when long time is lasted for, and it employs.

[0039]

In addition, By this arrangement, it is distress that irradiate ultraviolet radiation over the whole sample surface of audacious behavior product uniformly.

[0040]

However, even if irradiation of ultraviolet radiation is done after accretion of *dopanto* as had shown in experiment 2, as indicated in FIG. 3, it is put in large-scale chamber 301 by being effective in, and light source 312 is established in spaced-apart location from cathode 304, anode 303 is moved in location of light source 313 after sputtering, and ultraviolet radiation may be irradiated.

[0041]

In FIG. 3, a thing of equivalence is available for vacuum pump 302, anode 303, cathode 304, sample 305, heater 306, power source 308, target 309, bomb 310, mass flow controller 311 and butterfly valve 314 for vacuum pump 102 shown in each FIG. 1, anode 103, cathode 104, sample 105, heater 106, power source 108, target 109, bomb 110, mass flow controller 111 and butterfly valve 114 and parenchyma. In the event of particularly large-scale apparatus, design is easy constructive FIG. 3. In addition, When a doped layer is wanted to do thick, sputtering is not continued so for a long time at a time, gyrus had better repeat plural this dislodging.

[0042]

[EXAMPLE]

Semiconductor buttering method of the present invention and embodiment of a device are described the following, and, even more particularly, the present invention is explained, but, the present invention is not a thing limited the several class to by this.

[0043]

Apparatus shown in FIG. 1 was used, and, in the example 1 present embodiment, pin type a-Si photoelectromotive force element 408 of lamination shown in cross section scheme of FIG. 4 was made. This photoelectromotive force element 408 is bottom electrode 402, n type semiconductor layer 403, i mold semiconductor layer 404, p pattern semiconductor layer 405, transference electrode 406 and the photoelectromotive force element which it accumulates in this order, and formed syuden electric pole 407 on basal plate 401. In addition, It is assuming incidence of glow being done than side of transference electrode 406 with photoelectromotive force element 408 of the present embodiment.

[0044]

At first, Angle type basal plate made by stainless (5cm * 5cm) is set in commercial *supatta* apparatus (a product made in Ulvac company, SB H -2206 DE), Ag (99.99%) is used as target, and, in addition, in Ag film of 0.3 μm , Zn O (99.9%) is used as target in succession, and *supatta* deposits Zn O film of 1.5 μm , bottom electrode 402 was formed.

[0045]

Sequentially, Formed basal plate of this bottom electrode 402 was set in commercial plasma CVD apparatus (product made in Ulvac company, CHJ-3030). In draw off pump, air release pipe of reaction vessel was gone through, and a wild pull, high vacuum were pulled, and it was operated. Then, The skin temperature of basal plate controlled by temperature control mechanism to become 250 degrees Celsius.

[0046]

In the event that exhaust was done enough, Si H₄ 300sccm, Si F₄ 4sccm, P H₃ /H₂ (1% H₂ attemperation) 55sccm, H₂ 40sccm are introduced than gas introduction pipe, valve lift of throttle valve is adjusted, and internal pressure of reaction vessel is held in 1Torr, pressure was stable, and electric power of 200W was cast than a high frequency source promptly. The plasma made last for five minutes. By this, n⁺ a-Si as n⁺ semiconductor layer 403: H: F film is formed on bottom electrode 402.

[0047]

After having exhausted again, Si H₄ 300sccm, Si F₄ 4sccm, H₂ 40sccm are introduced than gas introduction pipe this time, valve lift of throttle valve is adjusted, and internal pressure of reaction vessel is held in 1Torr, pressure was stable, and electric power of 150W was cast than a high frequency source promptly. The plasma made last for 40 minutes. By this, a-Si as i type semiconductor layer 404: H: F film is formed on n type semiconductor layer 403.

[0048]

Next, Basal plate 401 is taken out than plasma CVD apparatus, it set in doping apparatus shown in FIG. 1. Boron (B), as target, Ar discharge 5sccm, 2*10< pressure S UP> While irradiating ultraviolet radiation under conditions of three Torr, basal plate temperature 100 degrees Celsius, discharge electric power 200W, discharge is continued for 70 seconds, p pattern semiconductor layer 405 is formed on i pattern semiconductor layer 404.

[0049]

Next, Transference electrode 406 (IT O (In₂ O₃ +SnO₂)) is formed by metallizing, even more particularly, it was masked, and syuden electrode 407 (Al) was deposited, and photoelectromotive force element 408 was finished.

[0050]

9.3% were provided in photoelectric conversion efficiency (η) when characterization was done about made photoelectromotive force element 408 in 1.5 (100mW/cm²) air trout (it is written down with AM) glow irradiation bottoms. In addition, Less than 20% were fitted into when alteration rate as opposed to initial value of photoelectric conversion efficiency after continuous irradiation was measured for 500 hours of AM1.5 (100mW/cm²) glow.

[0051]

Roll two roll apparatus 542 shown in FIG. 5 was used, and, in the example 2 present embodiment, a-Si/a-Si tandem photoelectromotive force element 613 of lamination shown in cross section scheme of FIG. 6 was made.

[0052]

Even more particularly, n type semiconductor layer 603 that this photoelectromotive force element 613

composes bottom electrode 602, the first cell 611 on basal plate 601, i mold semiconductor layer 604, p pattern semiconductor layer 605, n pattern semiconductor layer 606 which, even more particularly, compose the second cell 612, i pattern semiconductor layer 607, p pattern semiconductor layer 608 are transference electrode 609 and the photoelectromotive force element which they accumulate in this order, and formed *syuden* electric pole 610. In addition, It is assuming incidence of glow being done than side of transference electrode 609 with photoelectromotive force element 613 of the present embodiment.

[0053]

It is serial, and roll two roll apparatus 542 of FIG. 5 forms photoelectromotive force element to cingulate basal plate 504 made by rustless steel. Apparatus of the figure above winds basal plate export chamber 503, the first n pattern chamber 513, the first i pattern chamber 522, the first p pattern chamber 532, the second n pattern chamber (not shown), the second i pattern chamber (not shown), the second p pattern chamber (not shown) and basal plate off, and chamber 539 is disposed by this order. The second n type chamber, the second i type chamber, the second p mold chamber are n pattern chamber 513 of the first each, the first i pattern chamber 522, constitution at all the same as the first p pattern chamber 532. Each chamber interval is isolated by gas gate 507,515,524,533,536 (other non-graphic display), contamination of impurity between chamber is prevented.

[0054]

At first tenioid basal plate 504 is set chamber, and while it is layered, guide roller 505 is gone through from this chamber, and basal plate is serial, and basal plate export chamber 503 is carried out in the figure above to reaction chamber. In addition, Air exit 502 and bulb 501 is gone through, and evacuation can be left. Basal plate tenioid basal plate 538 that it is wound off, and chamber 539 is layered is chamber wound off, and guide roller 537 is gone through, and basal plate is serial, and it is carried in to this chamber by reaction chamber while it is layered. In addition, Air exit 540 and bulb 541 is gone through, and evacuation can be left.

[0055]

It is plasma CVD chamber, and n type chamber 513 and i type chamber 522 accumulates in each n pattern semiconductor layer and i pattern semiconductor layer. Basal plate is heated with basal plate heat heater 514,523 in each chamber 513,522, and it is controlled by predetermined basal plate temperature. Charge stock gas is supplied than charge stock gas supply pipe 510,518, current is fixed by shielding board 512,521, is disassembled occurrence between cathode 511,520 and basal plate by done plasma, and semiconductor membrane is formed on basal plate, even more particularly, is exhausted than air exit 509,519.

[0056]

p type chamber 532 is embodiment of doping apparatus of the present invention with the use of method of the present invention. Basal plate is controlled with basal plate heat heater 531 by predetermined temperature. Chamber internal is done evacuation of than air exit 528. Target 530 of boron (B) is set in face of cathode 529. Basal plate functions as anode with this roll two roll apparatus 542, and plasma can leave occurrence between cathode 529. Light source 530 of ultraviolet radiation comprises alongside of cathode, after at first was accumulated *dopanto* on i pattern semiconductor layer with dislodging of basal plate, ultraviolet radiation is irradiated, and *dopanto* becomes activate. By this assembling, Continuous duty of ultraviolet light source for long time is enabled. Ar is supplied than charge stock gas supply pipe 527.

[0057]

Sweep gas such as Ar, hydrogen is introduced into gas gate 507,515,524,533,536 (other non-graphic display) than gas admission port 506,508,516,517,525,526,534,535 (other non-graphic display) to isolate gas between chamber.

[0058]

Photoelectromotive force element 613 was made by means of such roll two roll apparatus 542.

[0059]

At first, Tenioid basal plate made by rustless steel is set in stepless *supatta* apparatus (not shown), Al-Si (5% Si) is used as target, and, in addition, in Al-Si film of 0.2 μm , Sn O_2 (99.99%) is used as target in succession, and *supatta* deposits Sn O_2 film of 0.1 μm , bottom electrode 602 was formed.

[0060]

Sequentially, It set to roll two roll apparatus 542 which formed tenioid basal plate of this bottom electrode 602 was shown in FIG. 5. Afterwards, In draw off pump (not shown), air release pipe of each chamber was gone through, and vacuum was pulled, and it was operated. Then, The skin temperature of

basal plate controlled by temperature control mechanism to become 250 degrees Celsius.

[0061]

In the event that exhaust was done enough, Ar gas is introduced into p pattern chamber, gas gate with $\text{SiH}_4/\text{SiF}_4/\text{H} < \text{S U B} > < / \text{S U B} >_2$ in i pattern chamber with $\text{SiH}_4/\text{PH}_3/\text{H}_2$ in n pattern chamber than gas introduction pipe 510,518, the pressure of in 100mTorr and p pattern chamber held internal pressure of n pattern and i pattern chamber in 50mTorr.

[0062]

Pressure was stable, and electric power is spent than each high frequency source, occurrence put plasma in each chamber and light source is illuminated, it makes discharge was stable, and transport cingulate basal plate from left side to right side direction out of figure in transportation speed 20cm/min, lamination formed n, i, p, n, i, p pattern semiconductor layer in succession.

[0063]

After semiconductor layer was laminated by full length of tenioid basal plate, and having formed, it is taken out after cooling, it sets in IT O ($\text{In}_2\text{O}_3 + \text{SnO}_2$) continuation vapor deposition apparatus (not shown), and cingulate basal plate full length is lasted for, and IT O layer of thickness 700A is deposited, it was done with transference electrode 609. Even more particularly, It continued, and a solar cell module of 35cm * 70cm was made in stepless apparatus (not shown) to modularize.

[0064]

Higher than 8.0% are provided in photoelectric conversion efficiency (η) when characterization is done about a made solar cell module in an AM1.5 ($100\text{mW}/\text{cm}^2$) glow irradiation bottom, the variation of characteristic between module fitted into less than 7% more.

[0065]

In addition, Less than 16% were fitted into when alteration rate as opposed to initial value of photoelectric conversion efficiency after continuous irradiation was measured for 500 hours of AM1.5 ($100\text{mW}/\text{cm}^2$) glow.

[0066]

These modules were connected, and power supply system of 1kW was able to be made.

[0067]

For comparative purposes, higher than photoelectric conversion efficiency (η) 7.8% are provided when the photoelectromotive force element which is similar is made without diverting sweep gas to each gas Kate, the degradation factor after 500 hours fitted into less than 18%. In other words, Even if sweep gas was not used, some effect of diffusion of *dopanto* between each chamber was minor although it was recognized.

[0068]

Apparatus (not shown) that remodeled roll two roll apparatus 542 shown in FIG. 5 partly was used, and, in the example 3 present embodiment, an a-Si/a-Si tandem photoelectromotive force element of lamination shown in cross section scheme of FIG. 6 was made same as example 2. It is a thing with the use of doping apparatus of the same present invention of p mold chamber and *zen* of the first or the second in the second n type chamber that is different from apparatus of FIG. 5.

[0069]

Target of antimony (Sb) is used in in target of boron (B) and the second n mold chamber in the first and the second p type chamber.

[0070]

Photoelectromotive force element 613 was made by means of such a roll two roll apparatus.

[0071]

At first, Tenioid basal plate made by rustless steel is set in stepless *supatta* apparatus same as example 2. Al-Si (5% Si) is used as target, and, in addition, in Al-Si film of 0.5 μm , Zn O (99.99%) is used as target in succession, and *supatta* deposits Zn O film of 0.5 μm , bottom electrode 602 was formed.

[0072]

Sequentially, Formed tenioid basal plate of this bottom electrode 602 was set in roll two roll apparatus of the present embodiment. Afterwards, In draw off pump, air release pipe of each chamber was gone through, and vacuum was pulled, and it was operated. Then, The skin temperature of basal plate controlled by temperature control mechanism to become 250 degrees Celsius.

[0073]

In the event that exhaust was done enough, Ar gas is introduced into the first, the second p pattern chamber and the second n pattern chamber, gas gate with $\text{SiH}_4/\text{SiF} < \text{S U B} > < / \text{S U B} >_4/\text{H}_2$ in i

pattern chamber of the first and the second with $\text{SiH}_4/\text{PH}_3/\text{H}_2$ in the first n pattern chamber than gas introduction pipe, valve lift of throttle valve was adjusted, and in 100mTorr and the second n pattern chamber and the first, the pressure of the second p pattern chamber held the first n pattern and the first, internal pressure of the second i pattern chamber in 50mTorr. Pressure was stable, and light source of each p type chamber is lighted, electric power is cast than each high frequency source, and occurrence put plasma in chamber of each, and it makes discharge was stable, and transport circulate basal plate in transportation speed 20cm/min, lamination formed n, i, p, n, i, p pattern semiconductor layer in succession.

[0074]

After semiconductor layer was laminated by full length of tenioid basal plate, and having formed, it is taken out after cooling, even more particularly, IT O ($\text{In}_2\text{O}_3 + \text{SnO}_2$) layer is deposited, and transference electrode 609 is formed, continuation made solar battery module of 30cm * 120cm in the apparatus which modularized continuation. Higher than 8.5% are provided in photoelectric conversion efficiency (η) when characterization is done about a made solar cell module in an AM1.5 (100mW/cm²) glow irradiation bottom, even more particularly, the variation of characteristic between module fitted into less than 10%.

[0075]

In addition, Less than 15% were fitted into when alteration rate as opposed to initial value of photoelectric conversion efficiency after continuous irradiation was measured for 500 hours of AM1.5 (100mW/cm²) glow.

[0076]

Apparatus (not shown) that remodeled roll two roll apparatus 542 shown in FIG. 5 partly was used, and, in four embodiment embodiment, a-SiC/a-Si/a-SiGe triple pattern photoelectromotive force element of lamination shown in cross section scheme of FIG. 7 was made. Apparatus used in the present embodiment is the thing which, even more particularly, added n pattern of tertiary, i pattern and p pattern chamber to apparatus used in example 2, and terrible - pinguchanba of the present invention, chamber of other are plasma CVD chamber only p pattern chamber of tertiary from the first.

[0077]

Photoelectromotive force element 717 shown in FIG. 7 was made by means of such a roll two roll apparatus.

[0078]

Even more particularly, n type semiconductor layer 703 that this photoelectromotive force element 717 composes bottom electrode 702, the first cell 714 on basal plate 701, i pattern semiconductor layer 704, p pattern semiconductor layer 705, n pattern semiconductor layer 706 which, even more particularly, compose the second cell 715, i pattern semiconductor layer 707, p pattern semiconductor layer 708, n pattern semiconductor layer 709 which, even more particularly, compose cell 716 of tertiary, i pattern semiconductor layer 710, p pattern semiconductor layer 711 are transference electrode 712 and the photoelectromotive force element which they accumulate in this order, and formed syuden electric pole 713. In addition, It is assuming incidence of glow being done than side of transference electrode 712 with photoelectromotive force element 717 of the present embodiment.

[0079]

At first, Tenioid basal plate made by rustless steel is set in stepless *supatta* apparatus same as example 2, Al (99.9%) is used as target, and, in addition, in Al film of 0.3 μm , Zn O (99.99%) is used as target in succession, and *supatta* deposits Zn O film of 0.3 μm , bottom electrode 702 was formed.

[0080]

Sequentially, Formed tenioid basal plate of bottom electrode 702 was set in roll two roll apparatus. Afterwards, In draw off pump, air release pipe of each chamber was gone through, and vacuum was pulled, and it was operated. Then, The skin temperature of basal plate controlled by temperature control mechanism to become 250 degrees Celsius.

[0081]

In the event that exhaust was done enough, Ar gas is introduced into with 4/ SiH_4/CH_4 and each p pattern chamber, gas gate in i pattern chamber of tertiary with $\text{SiH}_4/\text{SiF}_4/\text{H}_2$ in the second i pattern chamber with $\text{SiH}_4/\text{GeH}_4/\text{H}_2$ in the first i pattern chamber with $\text{SiH}_4/\text{PH}_3/\text{H}_2$ in each n pattern chamber than gas introduction pipe, valve lift of throttle valve was adjusted, and the pressure of in 100mTorr and each p pattern chamber held internal pressure of each n pattern and each i

pattern chamber in 50mTorr.

[0082]

Pressure was stable, and light source of each p type chamber is lighted, electric power is cast than each high frequency source, and occurrence put plasma in chamber of each, and it makes discharge was stable, and transport cingulate basal plate in transportation speed 30cm/min. lamination formed n. i. p. n. i. p pattern semiconductor layer in succession.

[0083]

After semiconductor layer was laminated by full length of tenioid basal plate, and having formed, it is taken out after cooling, even more particularly, IT O ($\text{In}_2\text{O}_3 + \text{SnO}_2$) layer is deposited, and transference electrode 609 is formed, continuation made solar battery module of 30cm * 120cm in the apparatus which, even more particularly, modularized continuation.

[0084]

Higher than 10.2% are provided in photoelectric conversion efficiency (η) when characterization is done about a made solar cell module in an AM1.5 (100mW/cm²) glow irradiation bottom, even more particularly, the variation of characteristic between module fitted into less than 5%.

[0085]

In addition, Less than 8% were fitted into when alteration rate as opposed to initial value of photoelectric conversion efficiency after continuous irradiation was measured for 500 hours of AM1.5 (100mW/cm²) glow.

[0086]

These modules were connected, and power supply system of 5kW was able to be made.

[0087]

Constructive polycrystal Si solar cell 801 as shown in FIG. 8 is described in five embodiment embodiment. A n type polycrystal Si wafer of a diameter of 6 inches that face made in Wacker company was ground (resistivity 2ohm / cm) was prepared for as basal plate. After having removed natural oxidation film in *doru* acid, it is configuration same as doping apparatus of FIG. 1 in this basal plate, but, to come to official polishing face in large-scale doping apparatus, it set. Plate of Ga of fineness 99.9% was used for target 109. For doping condition, Ar discharge 20sccm, 10< pressure S UP> Three Torr, basal plate temperature 100 degrees Celsius, discharge electricity are done with 1kW, exposure of ultraviolet radiation, discharge were continued for 150 seconds, and p pattern domain 802 was formed. Subsequently, Target 109 is changed for plate of Sb of fineness 99.9%, n⁺ pattern domain 803 was formed in similar doping condition except that basal plate was reset inside out. This n⁺ mold territory 803 forms so-called back Sir festival field, and recombination electric pole around carrier is prevented, it is a thing, even more particularly, to improve *omikku* characteristics. Subsequently, Ti, Pd, *syuden* electrode 804 comprising of laminating of Ag, bottom electrode 805 were formed by electron beam evaporation method on both sides. Ectal electrode hung face mask not to disturb incidence of glow very much, and grid was done if-shaped. After having formed electrode, a sintering ring was gone at 400 degrees Celsius for two minutes. Subsequently, Zn S and Mg F₂ was laminated, and it was assumed anti-reflective layer 806.

[0088]

Photoelectric conversion efficiency (η) was full of with 15.24 % 0.61%, and superior characteristic and homogeneity were provided when this sample was cut in 2cm angle, and solar cell character was evaluated.

[0089]

Six embodiment embodiment is example of the a-Si film transistor which shows the cross section configuration in FIG. 9 (TFT). Cr is deposited for basal plate 901 in 7059 coning # glass on this top, even more particularly, gate 902 was formed in *fuotorisogurafi* operation. Subsequently, It accumulated with amorphous nitriding silicon (a-SiN) membrane 903 of thickness 3000A as charge stock gas in Si H₄ and ammonia (NH₃) in commercial capacity bond type high frequency glow discharge device. It accumulated on this top with i type a-Si layer 904 of caliper 2000A by means of the same apparatus. It accumulated, and channel 905 was left, and a-SiN layer of caliper 3000A was etched in *fuotorisogurafi* operation in the same apparatus again on this top. When sample was used with embodiment 5 after this, it sets in similar doping apparatus, and plate of P of purity 99% is used as target, as doping condition, exposure of ultraviolet radiation, discharge were continued for quantity of flow 30sccm of Ar, 5*10 pressure ^{-3s} Torr, basal plate temperature 80 degrees Celsius, discharge electric power 800W for 200

seconds, and n^- pattern domain 906 was formed. Because a-SiN of channel 905 is insulating material here, it does not need to be possible for low resistance territory by doping in face. Subsequently, Caliper 2000A deposit Al on this top, channel 905 more was etched in *fuorisogurafi* operation, and TFT was formed for sauce 907, drain 908. In addition, Channel length 10 is μm here. In this way, Each conductor was adhered to gate 902 of produced TFT, sauce 907, drain 908, and field of 20cm angle was lasted for, and transistor characteristic was evaluated. At the time of drain tension 15V, ON/OFF ratio 1.5×10^5 with gate tension 15V and 0V were superior with five time \downarrow 8%. Because a channel section is protected in a-SiN, and disposal of etch is not received in method of the present invention, it is thought ON/OFF ratio is massive and that homogeneity is superior. Therefore, TFT by method of the present invention is optimum to use in active matrix circuit of a large-sized liquid crystal display.
[0090]

[EFFECT OF THE INVENTION]

According to the doping method of the present invention and the device, big as against ground material of the semiconductor which is good quality, doping do without damaging and because aftertreatment in high temperature is unnecessary, *o* which is monocrystal, polycrystal, amorphous is not asked, as against various semiconductor, semiconductor regions of superior p pattern of characteristic or n pattern can be formed. Besides, Superior semiconductor devices of character can be got so that there is not unnecessary diffusion of *dopanto*. In addition, Constitution of apparatus is simple, and the characteristic which is homogeneity is provided over audacious behavior product, because treatment time is had a short, particularly large-scale solar battery or active matrix circuit of a liquid crystal display can be produced in cost low.

[BRIEF DESCRIPTION OF DRAWINGS]

[FIG. 1]

It is outline block diagram to show embodiment of terrible - *pingu* apparatus of the preferred present invention in to carry out terrible - *pingu* method of the present invention.

[FIG. 2]

It is cross section * equation figure showing a-Si solar cell made in terrible - *pingu* method of the present invention.

[FIG. 3]

It is outline block diagram to show embodiment according to a *thing* of terrible - *pingu* apparatus of the preferred present invention in to carry out terrible - *pingu* method of the present invention.

[FIG. 4]

It is section * formula figure to show single mold a-Si solar cell made in terrible - *pingu* method of the present invention in.

[FIG. 5]

It is outline block diagram showing an example of the *ro - rutouro - ru* apparatus which incorporated terrible - *pingu* apparatus of the present invention.

[FIG. 6]

It is cross section * equation figure to show tandem a-Si solar cell made in terrible - *pingu* method of the present invention in.

[FIG. 7]

It is section * formula figure showing triple mold a-Si solar cell made in terrible - *pingu* method of the present invention.

[FIG. 8]

It is cross section * formula figure showing polycrystal Si solar cell made in terrible - *pingu* method of the present invention.

[FIG. 9]

It is cross section * type figure showing a-SiTFT made in terrible - *pingu* method of the present invention.

[DENOTATION OF REFERENCE NUMERALS]

101 Chamber 102 Vacuum pump 103 Anode 104 Cathode 105 Sample 106 Heater 107 Plasma 108 Power source 109 Target 110 Bomb 111 Mass flow controller 112.113 Light source

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

JP 05 024976

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The doping technique of the semiconductor which the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least is made to act on the front face of the aforementioned semiconductor, and dopes to the aforementioned semiconductor, making a dopant deposit on the surface of a semiconductor by the sputtering method using the target containing a dopant element.

[Claim 2] The doping technique of the semiconductor which the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least is made to act on this front face, and dopes to the aforementioned semiconductor after depositing a dopant on this front face by the sputtering method using the target containing a dopant element.

[Claim 3] The doping system of the semiconductor equipped with the chamber to which a semiconductor is set and in which evacuation is possible, the anode prepared in the interior of the aforementioned chamber, the cathode with which the target containing a dopant element was set to the front face, the power which supplies power to this cathode, the light source which irradiates the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least on the front face of the aforementioned semiconductor, and the line for supplying inert gas to the aforementioned chamber at least.

[Claim 4] The doping system of the semiconductor according to claim 3 equipped with a means to convey a semiconductor, between the positions which counter the light source which irradiates the position which counters a target, and a ultraviolet radiation.

[Translation done]

* NOTICE *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated
3. In the drawings, any words are not translated

DETAILED DESCRIPTION

[[Detailed Description of the Invention]]

[[0001]]

[Field of the Invention] This invention relates to the doping technique of the suitable semiconductor for the mass production of large area semiconductor devices, such as an active matrix circuit of the liquid crystal display of a highly efficient solar battery, and a doping system

[[0002]]

[Description of the Prior Art] There is the orientation of large-area-izing represented as flowing of the latest semiconductor-device technique in the active matrix circuit of a solar battery or a liquid crystal display with the orientation of detailed-izing represented by semiconductor memory and image sensors and integration. In a large area semiconductor device, it is necessary to lower the manufacturing cost per unit area as much as possible. Therefore, the semiconductor thin film of amorphous ***** deposited on cheap substrates, such as glass, a metal, and a ceramics, with the single crystal silicon wafer as a semiconductor material is beginning to use. However, in order to lower the manufacturing cost of a device, low-cost-ization is demanded about each of other manufacture process. Moreover, the manufactured device must have a uniform property over 30cm angle or the large area beyond it. That is, suitable process technique must be developed by it at a large area device.

[[0003]] Doping technique is mentioned as most important technique from the viewpoint of large-area-izing also in each manufacture process.

[[0004]] Most generally as doping technique of a semiconductor, the thermal diffusion method has been used. A thermal diffusion method is technique which usually diffuses in a semiconductor the dopant atom contained in the layer applied or deposited on the semiconductor front face at the elevated temperature of 1000 degrees C or more, and is activated as a dopant. Although this technique can be applied to a large area device comparatively easily, in order to use an elevated temperature, it faces using a thin film semiconductor and a constraint is received in an usable substrate. Moreover, processing takes a long time (usually several about hours), and the throughput of a manufacture is not good.

[[0005]] Moreover, there is the ion implantation method as other general doping techniques. It is the technique of accelerating by the electric field, devoting itself into a semiconductor, usually annealing about several hours at the temperature of 800 degrees C or more, and activating a dopant from the beam of the dopant atom ion ionized in the vacuum by this technique, after removing an impurity by the means of a mass analysis. Although it is easy to carry out a control of a dopant by this technique, it is necessary to scan a beam over a large area, and the throughput of a manufacture is not good too. Moreover, equipment becomes large-scale and becomes too disadvantageous in respect of a cost.

[[0006]] On the other hand, in the case of the thin film semiconductor deposited from a gaseous phase by technique, such as heat CVD and plasma CVD, there is the technique of mixing the gas which contains a dopant in a gaseous phase at the time of deposition of a thin film, and introducing a dopant atom into a thin film semiconductor. The property of the semiconductor of n type formed by this technique although it was good for large-area-izing to also have been comparatively easy and to also have compared a throughput with a thermal diffusion method or the ion implantation method, or p type was not necessarily enough, and the application to a semiconductor device had many inadequate things. It becomes what was inferior compared with the case where the crystal grain of Si will especially become small by high concentration if a phosphorated hydrogen (PH₃) tends to be mixed to the mono silane (SiH₄) of a raw material in case polycrystal Si is deposited with heat CVD as an example known well, and it is going to make it n type, and the property as n type Si makes it n type by the thermal-diffusion-method and ion in plastic ***** method. Moreover, in case an amorphous silicon (a-Si) is deposited by the plasma CVD method, it is SiH₄ of a raw material. If a diboron hexahydride (B₂H₆) tends to be mixed and it is going to make it p type, an optical band gap (E_g) falls, a localized level will increase and the property as a p type semiconductor will become what was inferior.

[[0007]] If the gas containing a dopant is mixed in a gaseous phase as the ground, the reaction of the gas containing the elements (Si etc.) of the principal component which

constitutes a semiconductor will be affected, and it will be considered for changing the precursor (precursor of a deposition reaction) of deposition of a semiconductor [0008] Moreover, if it dopes by deposition, generally, the semiconductor field of n type or p type cannot be alternatively formed in the specific location on a substrate. For this reason, a process is complicated especially in the application to a liquid crystal display. Some proposals are made from such a viewpoint.

[0009] M.B. Spitzer and S.N. Bunker. The ion implantation of ^{31}P which does not perform a mass analysis to p type single crystal Si was performed, and the solar battery of 1.5% of the conversion efficiencies with pin junction was made (19th I.I.E. Photovoltaic Conf. San Diego and 1982p 711-7) H. Hoch etc. made the solar battery of 10% of conversion efficiencies without the acid-resisting layer by the same technique (Proc 3rd PVSI'82 in Japan (82) p 7-7) By the ion in plastic ***** method do not perform a mass analysis, equipment becomes comparatively easy, and its throughput of a manufacture also improves. However, in applying to a solar battery, processing of the large area of sufficient like is difficult. Moreover, after driving in ion in their experiment, the annealing is performed above 550 degrees C or 600 degrees C, and there are many constraints to the application to the throughput of a manufacture being not only low but a thin film semiconductor.

[0010] Moreover, S.D. Westbrook etc. decomposes the gas containing boron (B) by glow discharge, after accelerating boron ion and devoting oneself to n type single crystal Si by impressing the electric field further, performs annealing above 550 degrees C, and is making the solar battery of no less than 19% of conversion efficiencies (Appl. Phys Lett Vol 50 (87) p 469-). On the other hand, Yoshida, Seisuke, and Hiroo perform doping to a-Si of 1 μm using the same equipment, and are making the thin film transistor (11-11: J. Vac Device Lett Vol 9 (1988) p 90-). By such technique, it is easy to carry out large area-ization, and the throughput of a manufacture is also comparatively good. Moreover, a p type or n type field can be alternatively formed in the specific location of a semiconductor side as the latter is shown. However, in order not to perform a mass analysis, various kinds of unnecessary ion will also be driven in at high speed in addition to dopant ion. Therefore, especially when annealing at sufficient

temperature was difficult a-Si, it was hard to remove the damage by ion, and it had become the failure which gets poisoned by the application to an a-Si solar battery. Moreover, about a neutral dopant atom except ion, a control is impossible, and it is easy to diffuse these dopant atoms to each part of equipment. Especially, in the a-Si solar battery, the pin junction is usually used, and it consists of six layers and nine layers from three n type, i type, and p type layers at least in the tandem-like a-Si cell which carried out the laminating of further two or more pin junctions. These dopants will tend to have a bad influence on the property of a device, if it mixes in the semiconductor layer (especially i layers) from which an adjoining conductivity type is different. With the roll-to-roll equipment which performs continuity deposition to a long band-like substrate for the purpose of the mass production of an a-Si solar battery especially, a diffusion of the dopant to an adjoining membrane formation room tends to happen.

[0011] Thus, in order to mass-produce a highly efficient a-Si solar battery, the doping technique to a large area needs to be improved further. Moreover, also in the case of the crystal semiconductor solar battery and the liquid crystal display, the development of the good doping technique of the throughput of a manufacture was desired.

[0012] [Problem(s) to be Solved by the Invention] this invention is made in view of such present condition, and an unnecessary diffusion of a dopant is easy few equipment in a manufacture of a semiconductor device. In the semiconductor of p type which was excellent in the property, or n type, homogeneity is good over a large area. The equipment for enforcing the technique of manufacturing by the short processing time and this technique is offered, and especially, the manufacture by the low cost of the semiconductor device of a large area like a highly efficient solar battery or a liquid crystal display is enabled, and it aims at contributing to the spread of these devices.

[0013] [Means for Solving the Problem] It is making to form the field of the semiconductor of p type with a good property, or n type by irradiating a ultraviolet radiation on the surface of a semiconductor, and activating a dopant in the operation, in case this invention deposits a dopant layer by the sputtering method on the surface of a semiconductor into main point.

[0014] That is, making a dopant deposit on the surface of a semiconductor by the sputtering method using the target containing a dopant element, it makes the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least act on the front face of the aforementioned semiconductor, and the doping technique of the semiconductor of this invention dopes to the aforementioned semiconductor.

[0015] Moreover, after the doping technique of the semiconductor of this invention deposits a dopant on this front face by the sputtering method using the target containing a dopant element, it makes the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least act on this front face, and dopes to the aforementioned semiconductor.

[0016] The doping system of the semiconductor of this invention is equipped with the chamber in which the evacuation with which a semiconductor is set is possible on the other hand, the anode prepared in the interior of the aforementioned chamber, the cathode with which the target containing a dopant element was set to the front face, the power which supplies power to this cathode, the light source which irradiates the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least on the front face of the aforementioned semiconductor, and the line for supplying inert gas to the aforementioned chamber at least.

[0017] Furthermore, the doping system of the semiconductor of this invention should be equipped with a means to convey a semiconductor, between the positions which counter the light source which irradiates the position which counters a target, and a ultraviolet radiation.

[00018]

[function] Drawing 1 is an outline block diagram showing the embodiment of the doping system of a suitable this invention to enforce the doping technique of this invention.

[00019] In the chamber 101 in which evacuation is possible, one pair of electrodes of the anode 103 and the cathode 104 are prepared by the vacuum pump 102. The sample 105 is set to the anode 103.

[00020] The polycrystal and the amorphous semiconductor thin film which were deposited on substrates, such as a semiconductor wafer of a single crystal or a polycrystal and a glass metallurgy group, as a sample are used. These semiconductors may be beforehand doped according to the purpose, and do not need to be doped. A sample 105 can be heated to desired temperature at a heater 106. The cathode 104 is connected to the power 108 for occurring a plasma 107 between an anode 103 and the cathode 104. The target 109 is set on the cathode 104. As a material of a target, B, aluminum, Ga, In, Ti, P, As, Sb, Bi, etc. are used. A RF generator is sufficient although DC power supply are sufficient as power 108, especially -- a target material -- high -- when ****, the power of radio frequencies, such as 13.56 etc. MHz, can use it suitably inert gas, such as Ar, is introduced into a chamber 101 from a bomb 110. The flow rate of inert gas is adjusted by the mass-flow controller 111. And the pressure in a chamber 101 is adjusted by the opening of the mass-flow controller 111 and the butterfly valve 114. Moreover, in the chamber 101, the mercury-vapor lamp 112,113 (it is henceforth described as the light source 112,113) is further formed as light source of a ultraviolet radiation, and the front face of a sample 105 can be irradiated now at any time.

[00021] The following experiments were conducted in order to check a one experiment effect of the invention: p type Si wafer (1 ohm of specific resistances, cm) which carried out the sintering of the golden electrode to the rear face was made into the sample 105, and it set to the doping system of drawing 1. Once exhausting the inside of a chamber 101 to 10⁻⁶ Torr, Ar was passed 5 secms, the butterfly valve 114 was adjusted, and the pressure was set to 10⁻³ Torr. Subsequently, the current of a heater 106 was adjusted so that substrate temperature might become 100 degrees C. As a target 109, the plate of the simple substance of P of 99.9% of purity was used. Subsequently, the light source 112,113 was turned on. When the RF power of 200W was supplied, adjusting a non-illustrated matching circuit so that reflective power may serve as the minimum from power 108 in this status, the plasma 107 occurred. Supply of the power to power 108, the light source 112,113, and the heater 106 was stopped in the place which passed for 100 seconds in this status. After the sample cooled, it took out from the inside of a chamber 101, started on 1cm square, and was referred to as sample 1A.

[00022] Next, the light source 112,113 was not turned on for the comparison, and also sample 1B was made from the completely same process as the above.

[00023] Next, lead wire was fixed with a silver paste on the rear face and front face of samples 1A and 1B. The volt ampere characteristic of both samples in the dark was measured first. At sample 1A, the rectification ratio in 1V is 3x10⁴. It was twice. By sample 1B, the rectification ratio was able to be taken only 50 times to it. Furthermore, the solar-battery property of both the samples in the basis of the solar simulator of the air mass (AM) 1.5 was seen. In sample 1A, the property good as a solar battery that 9.3% and an antireflection film do not have a conversion efficiency (eta) was acquired. On the other hand, sample 1B of the conversion efficiency (eta) was 1 the function as 2.7% and a solar battery 1 inadequate.

[00024] Except not turning on the light source 112,113 by experiment 2 view 1, after the same procedure as experiment 1 performed sputtering, the light source 112,113 was turned on for 10 minutes, and sample 2A was made. Moreover, the light source 112,113 was not turned on, but sputtering was performed for 50 seconds, subsequently

***** during 5 minutes was irradiated, sputtering and ultraviolet-radiation irradiation were repeated on the again same conditions, and sample 2B was made.

[00025] The rectification ratio of 1V in the dark is 2x10³ at sample 2A. In twice and sample 2B, it was 1x10⁵ times. Moreover, the conversion efficiency (eta) of sample 2A was 1 the conversion efficiency (eta) of sample 2B of the solar-battery property in AM1.5 18.5% 7.8%.

[00026] Since it was shown that experiment 3 this invention is effective also to an amorphous semiconductor, a solar battery which is shown in view 2 was made: commercial RF capacity-coupling type glow discharge equipment -- the stainless substrate 201 with a thickness of 1mm -- setting -- a this top -- the n-type-semiconductor layer 202 of a-Si -- subsequently the i-type-semiconductor layer 203 of a-Si was deposited. The creation conditions of the n-type-semiconductor layer 202 are 5% of P113 as material gas. Mixed Si14 it carries out in 5secms, pressure 0.5Torr, electric discharge power 50W, and substrate temperature of 250 degrees C, and a thickness is 200nm. The creation conditions of the i-type-semiconductor layer 203 are Si14 as material gas. It carries out in 20secms, pressure 0.5Torr, electric discharge power 100W, and substrate temperature of 250 degrees C, and a thickness is 4000nm. In this way, the sample was set to the equipment of drawing 1. The plate of the simple substance of B of 99.9% of purity was used as a target 109.

[00027] Having been referred to as Ar5secm, pressure 10⁻³Torr, the substrate temperature of 200 degrees C, and electric discharge power 200W, and turning on the light source 112,113 as doping conditions, electric discharge was continued for 50 seconds and p type field 204 was created.

[00028] After the sample cooled, it took out from the chamber 101, and it set to the commercial resistance heating type vacuum evaporation system, the vacuum evaporation of the alloy of In and Sn was carried out in the oxygen ambient atmosphere, the thickness 700nm deposition of the transparent electrode 205 of ITO (In2O3+SnO2) layer was done, and it was referred to as sample 3A. The sample which used the n-type-semiconductor layer 202 as the p type a-Si layer of thickness 200nm in drawing 2 was set to the doping system of drawing 1, and the P type field 204 was formed on the same doping conditions as the above using the target of P. The transparent electrode 205 was formed similarly and it was referred to as sample 3B.

[0029] The same procedure as experiment 1 estimated both the samples 3A and 3B. For the rectification ratio of 1 V, sample 3A is 1x10⁵. Twice and sample 3B are 8x10⁴. It was twice. Moreover, 8.5%, sample 3A is 7.8%, and, as for the conversion efficiency (eta) as a solar battery, sample 3B showed the property excellent in all.

[0030] Based on the above experimental result [device / of doping], it can guess as follows about the device of the method of doping this invention. In the sputtering method, although ion, such as Ar, exists in the plasma of electric discharge, these ion strikes the target 109 on the cathode 104 by which the bias is carried out to negative. The configuration atom of the target which recoils as a result accumulates on a sample 105. Generally a dopant atom will seldom invade to the interior of a sample, since it is neutral and it is not accelerated by the electric field. However, since it is combinable by the suitable coordination number finally [invade and] until the atom of a sample of a dopant is deep, in order to loosen a combination of Si which constitutes a semiconductor mutual [atomic] by the energy of the photon of a ultraviolet radiation, if a ultraviolet radiation is irradiated by the sample side, it is thought that it is activated as a dopant.

[0031] Therefore, since there is no damage like [at the time of driving in the ion with which a thermal diffusion called 100 degrees C was accelerated at high speed / can perform effective doping and / also in the low temperature which is not expectable at all], it is thought that the annealing as after treatment also becomes unnecessary.

[0032] Moreover, in heat (CVD) or a plasma (CVD) method, since the network of the parent of a semiconductor is formed without the bad influence of a dopant by the technique of this invention unlike the case where a semiconductor accumulates in the ambient atmosphere containing a dopant, it is expectable that formed p type layer and n type layer show the outstanding property.

[0033] Furthermore, in the case of the sputtering method, since a dopant atom starts skipping with a remarkable directivity toward a sample from a target, it is expectable that a diffusion of the dopant to the unnecessary location decreases sharply as gas compared with the case where a dopant is supplied.

[0034] The simple substance of a desired dopant element can be used as a material of the target used in enforcing the technique of this invention about a target. Namely, what is necessary is just to use the simple substance or alloy of P, As, Sb, and Bi with 4 group semiconductors, such as Si and germanium, in order to consider as p type and to use the simple substance or alloy of B, aluminum, Ga, In, and Tl as n type. Although the purity of these materials has the good higher one, generally at least its about 99% is usable by the mobility of impurity 99.9%. Moreover, although it is easy to use a plate-like thing as a configuration of a target, when the thing which pressed the powdered material, and a cathode are facing up, it is even good to have piled powder on the cathode.

[0035] Most generally Ar is used as a controlled atmosphere by the sputtering method about the controlled atmosphere of sputtering. Ar of an ionization rate is high and this is for hammering out a target atom most efficiently. However, for the purpose of doping, a not much big rate of sedimentation has that it is [much] unnecessary, and can also use inert gas, such as helium, Ne, Kr, and Xe, in addition to Ar.

[0036] The technique of this invention is applicable about doping conditions also not only to the semiconductor of four groups, such as Si, and germanium, its alloy, SiC, but compound semiconductors, such as GaAs and InP. However, a dopant is suitably chosen from the element of two groups, four groups, and six groups according to the semiconductor of a parent. The flow rate of inert gas, such as Ar, is suitably decided as gas of the ambient atmosphere of electric discharge according to a sample size. The pressure at the time of electric discharge is preferably set to 5x10⁻⁴ Torr to 0.1 Torr. 0.5 Torr from 1x10⁻⁴ Torr. Although electric discharge power is also decided according to a sample size, when it is the sample of 30cm angle, 5kW is preferably set to about 250W to 2kW from 100W. Although a good result may be obtained at a room temperature as substrate temperature, generally you may be 60 degrees C or more. In almost all cases, effect sufficient at about 200 degrees C is acquired.

[0037] As light used for irradiation about the irradiation technique of a ultraviolet radiation, the ultraviolet radiation with a wavelength of 250nm or less is still preferably effective 150nm or more 300nm or less wavelength. As light source, a commercial mercury-vapor lamp is used suitably. However, in air, since the light of such a wavelength field receives absorption and generates ozone, preparing into a vacuum chamber is desirable [the light source] like the doping system of drawing 1.

[0038] In the case of the doping system of drawing 1, since the light source 112, 113 is formed near the target 109, if it is used over a long time, dirt will adhere.

[0039] Moreover, it is difficult to irradiate a ultraviolet radiation uniformly over the whole sample from face of a large area with this configuration.

[0040] However, it prepares in the position which is distant from a cathode 304 in the light source 312 in the large-sized chamber 301 as it was shown in drawing 3, since it was effective even if it performs irradiation of a ultraviolet radiation after deposition of a dopant, as the experiment 2 was shown, an anode 303 is moved to the position of after sputtering and the light source 313, and it may be made to irradiate a ultraviolet radiation.

[0041] drawing -- three -- setting -- a vacuum pump -- 302 -- an anode -- 303 -- a cathode -- 304 -- a sample -- 305 -- a heater -- 306 -- power -- 308 -- a target -- 309 -- a bomb -- 310 -- a mass flow -- a controller -- 311 -- and -- a butterfly valve -- 314 -- respectively -- drawing -- one -- being shown -- a vacuum pump -- 102 -- an anode -- 103 -- a cathode -- 104 -- a sample -- 105 -- a heater -- 106 -- power -- 108 -- a target in especially large-sized equipment, the configuration of drawing 3 is easier for the design.

Moreover, it is better to seldom have continued sputtering at once for a long time but to repeat this move two or more times to thicken a dope layer.

[0042]

[Example] Although the semiconductor surface treatment technique of this invention and the example of equipment are described below and this invention is further explained to it, thereby, this invention is not limited at all.

[00043] In example 1 this example, the p n type a-Si photovoltaic cell 408 of the lamination shown in the cross section of drawing 4 was produced using the equipment shown in drawing 1. This photovoltaic cell 408 is a photovoltaic cell which carried out deposition formation of the lower electrode 402, the n-type-semiconductor layer 403, the i-type-semiconductor layer 404, the p type semiconductor layer 405, the transparent electrode 406, and the current collection electrode 407 on the substrate 401 at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 406 side in the photovoltaic cell 408 of this example.

[00044] First, the sputtering system (the UHVAC Corp. make, SKI-2206J) of marking of the square shape substrate made from stainless steel (5cmx5cm) -- setting -- Ag (99.999%) -- target ***** -- using -- 0.3-micrometer Ag thin film -- moreover, the sputter vacuum evaporator of the 1.5-micrometer / m thin film was carried out continuously, using / m (99.99%) as a target, and the lower electrode 402 was formed.

[00045] Then, the substrate in which this lower electrode 402 was formed was set to commercial plasma CVD equipment (the UHVAC Corp. make, CII-3030). The exhaust air pump performed a skimming and high-vacuum length operation through the exhaust pipe of a reaction container. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[00046] When exhaust air was fully performed, from the gas introduction spool, SiH₄ 300sccm, SiF₄ 4sccm, PH₃ / H₂55(1% H₂ dilution) sccm, and H₂ 40sccm were introduced, the opening of a throttle valve was adjusted, the internal pressure of a reaction container was held to 1 Torr, and the power of 200W was immediately switched on from the RF generator in the place by which the pressure was stabilized. The plasma was made to maintain for 5 minutes. Thereby, it is n+. The n+a-Si:H layer as a semiconductor layer 403 was formed on the lower electrode 402.

[00047] Immediately after exhausting again, SiH₄ 300sccm, SiF₄ 4sccm, and H₂ 40sccm were introduced from the gas introduction spool, the opening of a throttle valve was adjusted, the internal pressure of a reaction container was held to 1 Torr, and the power of 150W was switched on from the RF generator in the place by which the pressure was stabilized, this time. The plasma was made to maintain for 40 minutes. Thereby, the a-Si:H:F layer as a i-type-semiconductor layer 404 was formed on the n-type-semiconductor layer 403.

[00048] Next, the substrate 401 was taken out from plasma CVD equipment, and it set to the doping system shown in drawing 1. Boron (B) is used as a target, electric discharge is continued for 70 seconds, irradiating a ultraviolet radiation on condition that Ar flow rate 5sccm, pressure 2x10⁻³Torr, the substrate temperature of 100 degrees C, and electric discharge power 200W, and the p type semiconductor layer 405 was formed on the i-type-semiconductor layer 404.

[00049] Next, the transparent electrode 406 (ITO (In₂O₃+SnO₂)) was formed with vacuum deposition, the mask vacuum evaporator of the current collection electrode 407 (aluminum) was carried out further, and the photovoltaic cell 408 was completed.

[00050] About the produced photovoltaic cell 408, when the characterization was performed under air mass (it is heretoforth described as AM) 1.5 (100mW/cm²) light irradiation, 9.3% was obtained by the photoelectric conversion efficiency (eta). Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm²) light was measured, it ***** to less than 20%.

[00051] In example 2 this example, a-Si/a-Si tandem-die photovoltaic cell 613 of the lamination shown in the cross section of drawing 6 were produced using the roll-to-roll equipment 542 shown in drawing 5.

[00052] This photovoltaic cell 613 is the n-type-semiconductor layer 603 which constitutes the lower electrode 602 and the 1st cell 611 on a substrate 601, the i-type-semiconductor layer 604, the p type semiconductor layer 605, the n-type-semiconductor layer 606 that constitutes the 2nd cell 612 further, the i-type-semiconductor layer 607, the p type semiconductor layer 608, and a photovoltaic cell that carried out deposition formation of the transparent-electrode 609 and the current collection electrode 610 further at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 609 side in the photovoltaic cell 613 of this example.

[00053] The roll-to-roll equipment 542 of drawing 5 forms a photovoltaic cell in the band-like substrate 504 made from stainless steel continuously. As for the equipment of this drawing, the substrate send room 503, 1st n type chamber 513, 1st i type chamber 522, 2nd n type chamber (un-illustrating), 2nd i type chamber (un-illustrating), 2nd p type chamber (un-illustrating), and the substrate rolling-up room 539 are arranged at this order. 2nd n type chamber, 2nd i type chamber, and 2nd p type chamber are the completely same respectively configurations as 1st n type chamber 513, 1st i type chamber 522, and 1st p type chamber 532, between each chamber, it is isolated by the gas gates 507 and 515, 524, 533, 536 (others -- un-illustrating), and mixing of the impurity between chambers is prevented.

[00054] In this drawing, first, the substrate send room 503 is ** to which the band-like substrate 504 is set, and a substrate is continuously taken out through a guide roller 505 from this ** during membrane formation to a reaction chamber. Moreover, evacuation is carried out through the exhaust port 502 and the bulb 501. The substrate rolling-up room 539 is ** by which the formed band-like substrate 538 is rolled round, and a substrate is continuously carried in to this ** from a reaction chamber through a guide roller 537 during membrane formation. Moreover, evacuation is carried out through the exhaust port 540 and the bulb 541.

[00055] n type chamber 513 and i type chamber 522 are plasma CVD chambers, and deposit a n-type-semiconductor layer and a i-type-semiconductor layer, respectively. A substrate is heated at the substrate heating heater 514, 523 within each chamber 513, 522, and it is controlled by predetermined substrate temperature. It is supplied from the material gas supply pipe 510, 518, and flowing is prepared with the shield plate 512, 521, it is decomposed by the plasma which occurred between the cathode 511, 520 and the

substrate, a semiconductor layer is formed on a substrate, and material gas is further exhausted from an exhaust port 509, 519.

[0056] p type chamber 532 is the embodiment of the doping system of this invention. A substrate is controlled by the substrate heating heater 531 by predetermined temperature. Evacuation of the inside of a chamber is carried out from an exhaust port 528. The target 530 of boron (B) is set to the front face of a cathode 529. With this roll-to-roll equipment 542, a substrate functions as an anode and a plasma occurs between cathodes 529. After the light source 530 of a ultraviolet radiation is formed beside a cathode and a dopant deposits it on a i-type-semiconductor layer first in connection with a move of a substrate, a ultraviolet radiation is irradiated and a dopant activates it. By this configuration, the continuous duty of the ultraviolet light source covering a long time becomes possible. Ar is supplied from the material gas supply pipe 527.

[0057] In order to isolate the gas between chambers, sweep gas, such as Ar and hydrogen, is introduced into the gas gates 507 and 515, 524, 533, 536 (others -- un-illustrating) from gas inlets 506, 508, 516, 517, and 525, 526, 534, 535 (others -- un-illustrating).

[0058] The photovoltaic cell 613 was produced using such roll-to-roll equipment 542.

[0059] First, the band-like substrate made from stainless steel -- a continuity sputtering system (un-illustrating) -- setting -- aluminum-Si (5%Si) -- target ***** -- using -- a 0.2-micrometer aluminum-Si thin film -- moreover -- continuing -- SnO₂ (99.99%) -- target ***** -- using -- a 1-micrometer SnO₂. The sputter vacuum evaporation of the thin film was carried out, and the lower electrode 602 was formed.

[0060] Then, it set to the roll-to-roll equipment 542 in which the band-like substrate in which this lower electrode 602 was formed was shown in drawing 5. Then, the exhaust air pump (un-illustrating) performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[0061] When exhaust air was fully performed, in n type chamber, it is SiH₄ / PH₃ / H₂ from the gas introduction spool 510, 518. In i type chamber, it is SiH₄ / SiF₄ / H₂. Ar gas was introduced into p type chamber and the gas gate, and the pressure of p type chamber held again the internal pressure of n type and i type chamber to 100mTorr's at 50mTorr's.

[0062] In the place by which the pressure was stabilized, switched on power from each Rf generator, and made the plasma occur within each chamber, and turned on the light source, the band-like substrate was made to convey in the orientation of right-hand side from the left-hand side in drawing by conveyance speed 20cm/min in the place by which electric discharge etc. was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[0063] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, it took out after cooling, and it set to ITO (In₂O₃+SnO₂) continuity vacuum evaporation equipment (un-illustrating), the vacuum evaporation of the ITO layer of thickness 700nm was carried out covering the band-like substrate overall length, and it considered as the transparent electrode 609. Furthermore, continuity production of the 35cmx70cm solar-battery module was carried out with continuity modularization equipment (un-illustrating).

[0064] About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm²) light irradiation, 8.0% or more is obtained by the photoelectric conversion efficiency (eta), and the variation in the property between modules had ***** to less than 7% further.

[0065] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm²) light was measured, it ***** to less than 16%.

[0066] These modules were able to be connected and the 1kW electric power supply system was able to be produced.

[0067] When the photovoltaic cell same without passing sweep gas to each gas ***** because of a comparison was created, 7.8% or more of photoelectric conversion efficiencies (eta) is obtained, and the rate of a degradation of 500 hours after had ***** to less than 18%. That is, it was slight although the influence of a diffusion of the dopant between each chamber accepted a little even if it did not use sweep gas.

[0068] In example 3 this example, the roll-to-roll equipment 542 to which a-Si / a-Si tandem-die photovoltaic cell of the lamination shown in the cross section of drawing 6 like an example 2 are shown in drawing 5 was produced using the equipment (un-illustrating) converted in part. Having used the doping system of the 1st or 2nd p type chamber and the same this invention of ** for 2nd n type chamber differs from the equipment of drawing 5.

[0069] The target of boron (B) is used for the 1st and 2nd p type chambers, and the target of antimony (Sb) is used for 2nd n type chamber.

[0070] The photovoltaic cell 613 was produced using such roll-to-roll equipment.

[0071] First, the example 2 -- the same -- the band-like substrate made from stainless steel -- a continuity sputtering system -- setting -- aluminum-Si (5%Si) -- target ***** -- using -- a 0.5-micrometer aluminum-Si thin film -- moreover, the sputter vacuum evaporation of the 0.5-micrometer /nm thin film was carried out continuously, using ZnO (99.99%) as a target, and the lower electrode 602 was formed.

[0072] Then, the band-like substrate in which this lower electrode 602 was formed was set to the roll-to-roll equipment of this example. Then, the exhaust air pump performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become

250 degrees C.

[0073] the time of exhaust air fully being performed -- a gas introduction spool -- 1st n type chamber -- Si14 / P13 / H2 in the 1st and 2nd i type chambers, it is Si14 / Si14 / H2. Introduce Ar gas into the 1st and 2nd p type chamber and 2nd n type chamber, and the gas gate, and the opening of a throttle valve is adjusted. The pressure of 2nd n type chamber and the 1st and 2nd p type chamber held again the internal pressure of 1st n type and the 1st and 2nd i type chamber to 100mTorr at 50mTorr. In the place by which the pressure was stabilized, the light source of a each p type chamber was turned on, from each RF generator, switch on power, made the plasma occur within each chamber, the band-like substrate was made to convey by conveyance speed 20cm/min in the place by which electric discharge etc. was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[0074] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, further, it took out after cooling, and the vacuum evaporation of the TiO (In2O3+SnO2) layer was carried out, the transparent electrode 609 was formed and continuous production of the 30cmx120cm solar-battery module was carried out with continuity modularization equipment. About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm2) light irradiation, 8.5% or more is obtained by the photoelectric conversion efficiency (η), and the variation in the property between modules had ***** to less than 10% further.

[0075] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm2) light was measured, it ***** to less than 15%.

[0076] In example 4 this example, the roll-to-roll equipment 542 to which the a-SiC/a-Si/a-SiGe triple mold photovoltaic cell of the lamination shown in the cross section of drawing 7 is shown in drawing 5 was produced using the equipment (un-illustrating) converted in part. The equipment used by this example adds the 3rd n type, i type, and p type chamber to the equipment used in the example 2 further, and only the 1st to 3rd p type chamber of the doping chamber of this invention and other chambers is a plasma CVD chamber.

[0077] The photovoltaic cell 717 shown in drawing 7 using such roll-to-roll equipment was produced.

[0078] This photovoltaic cell 717 on a substrate 701, the lower electrode 702 and the 1st cell 714. The n-type-semiconductor layer 703 to constitute, the i-type-semiconductor layer 704, the p type semiconductor layer 705, the n-type-semiconductor layer 706 that constitutes the 2nd cell 715 further, the i-type-semiconductor layer 707, the p type semiconductor layer 708, the n-type-semiconductor layer 709 that constitutes the 3rd cell 716 further, the i-type-semiconductor layer 710. They are the p type semiconductor layer 711 and the photovoltaic cell which carried out deposition formation of the transparent electrode 712 and the current collection electrode 713 further at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 712 side in the photovoltaic cell 717 of this example.

[0079] First, the example 2 -- the same -- the band-like substrate made from stainless steel -- a continuity sputtering system -- setting -- aluminum (99.99%) -- target ***** -- using -- 0.3-micrometer aluminum thin film -- moreover, the sputter vacuum evaporation of the 0.3-micrometer ZnO thin film was carried out continuously, using ZnO (99.999%) as a target, and the lower electrode 702 was formed.

[0080] Then, the band-like substrate in which this lower electrode 702 was formed was set to roll-to-roll equipment. Then, the exhaust air pump performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[0081] the time of exhaust air fully being performed -- a gas introduction spool -- a each n type chamber -- Si14 / P13 / H2 1st i type chamber -- Si14 / Ge14 / H2 2nd i type chamber -- Si14 / Si14 / H2. In 3rd i type chamber, it is Si14 / Cl14/H2. Moreover, introduce Ar gas into a each p type chamber and the gas gate, and the opening of a throttle valve is adjusted. The pressure of a each p type chamber held again the internal pressure of every n type and a each i type chamber to 100mTorr at 50mTorr.

[0082] In the place by which the pressure was stabilized, the light source of a each p type chamber was turned on, from each RF generator, switch on power, made the plasma occur within each chamber, the band-like substrate was made to convey by conveyance speed 30cm/min in the place by which electric discharge was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[0083] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, it took out after cooling, and the vacuum evaporation of the TiO (In2O3+SnO2) layer was carried out, the transparent electrode 609 was formed and continuous production of the 30cmx120cm solar-battery module was further carried out with continuity modularization equipment.

[0084] About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm2) light irradiation, 10.2% or more is obtained by the photoelectric conversion efficiency (η), and the variation in the property between modules had ***** to less than 5% further.

[0085] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm2) light was measured, it ***** to less than 8%.

[0086] These modules were able to be connected and the 5kW electric power supply system was able to be produced.

[0087] The polycrystal Si solar battery 801 of a configuration as example 5 this example is shown in drawing 8 is explained. The n type polycrystal Si wafer (2 ohms of specific

resistances, cm) with which the front face made from Wacker was ground and which is the diameter of 6 inches was prepared as a substrate. After removing a natural-oxidation layer in fluoric acid, this substrate was set so that a polished surface might become a large-sized doping system with public although it was the same structure as the doping system of drawing 1. The plate of Ga of 99.99% of purity was used as a target 109. As doping conditions, Ar flow rate 20sccm, pressure 10-3 Torr, substrate temperature of 100 degrees C, and electric discharge power were set to 1KW, continued irradiation of a ultraviolet radiation, and electric discharge for 150 seconds, and formed p type field 802. Subsequently, it is n+ at the same doping conditions except exchanging a target 109 for the plate of Sb of 99.99% of purity, and having reset the substrate inside out. The type field 803 was formed. This n+ The type field 803 is for forming the so-called back surface field, preventing the recombination near the electrode of a carrier, and raising ohmic nature further. Subsequently, the current collection electrode 804 and the lower electrode 805 which become both sides from the laminating of Ti, Pd, and Ag were formed by the electron-beam-evaporation method. The surface electrode covered the mask and made it the shape of a grid so that the incidence of light might seldom be barred. After forming an electrode, the sintering was performed for 2 minutes at 400 degrees C. Subsequently, it is ZnS and MgF2 to a front face. The laminating was carried out and it considered as the acid-resisting layer 806.

[0088] When this sample was cut on 2cm square and the solar-battery property was evaluated, the property and homogeneity in which the photoelectric conversion efficiency (eta) was extremely excellent with 15.24**0.61% were acquired.

[0089] Example 6 this example is an example of the a-Si thin film transistor (TFT) which shows the cross-section structure in drawing 9. Corning #7059 glass was used as the substrate 901, on this, the vacuum evaporation of the Cr was carried out and the gate 902 was further formed at the photo-lithography process. Subsequently, it is SiH4 by commercial capacity-coupling type RF glow discharge equipment. The amorphous silicon-nitride (a-SiN) layer 903 of thickness 3000** was deposited for ammonia (NH3) as material gas. The i type a-Si layer 904 of thickness 2000** was deposited using the equipment same besides. The a-SiN layer of thickness 3000** was again deposited with the equipment same besides, and it left the channel 905, and etched at the photo-lithography process. It sets to the same doping system as what used the sample in the example 5 after this, and flow rate 30sccm of Ar, pressure 5x10-3 Torr, and the substrate temperature of 80 degrees C are continued as doping conditions, irradiation of a ultraviolet radiation and electric discharge are continued for 200 seconds as electric discharge power 800W, using the plate of P of 99.99% of purity as a target, and it is n+. The type field 906 was formed. Since a-SiN of a channel 905 is an insulator, the low resistance field by doping is not made on a front face by it here. Subsequently, on this, aluminum was carried out thickness 2000** vacuum evaporation, the channel 905 was further etched at the photo-lithography process, and TFT was formed as the source 907 and a drain 908. In addition, channel length is 10 micrometers here. Thus, lead wire was respectively fixed in the gate 902 of manufactured TFT, the source 907, and the drain 908, and transistor characteristics were evaluated over the domain of 20cm angle. (ON/OFF ratio with gate voltages 15V and 0V is 1.5x105 at the time of drain voltage 15V. It excelled with twice**8%. By the technique of this invention, in order that the channel section may be protected by a-SiN and may not receive processing of etching etc., (ON/OFF ratio is greatly considered that homogeneity is also excellent. Therefore, it is the best for using TFT by the technique of this invention for the active matrix circuit of a large-sized liquid crystal display.

[0090]

[Effect of the invention] According to the doping technique of this invention, and equipment, it can dope, without doing big trauma to the parent of a good semiconductor, and since the after treatment in an elevated temperature is unnecessary, it can be amorphous, and **** cannot be asked but a single crystal, polycrystal, p type that was excellent in the property, or an n type semiconductor field can be formed to various kinds of semiconductors. And since there is no unnecessary diffusion of a dopant, the semiconductor device which was excellent in the property can be obtained. Moreover, the configuration of equipment is easy, a uniform property is acquired over a large area, and since the processing time is short, a large-sized solar battery, the active matrix circuit of a liquid crystal display, etc. can be especially manufactured in a low cost.

[Translation done]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated
3. In the drawings, any words are not translated.

Field

[Field of the Invention] this invention relates to the doping technique of the suitable semiconductor for the mass production of large area semiconductor devices, such as an active matrix circuit of the liquid crystal display of a highly efficient solar battery, and a doping system.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1 This document has been translated by computer. So the translation may not reflect the original precisely.
- 2 **** shows the word which can not be translated.
- 3 In the drawings, any words are not translated.

1 technique

[Description of the Prior Art] There is the orientation of large-area-izing represented as flowing of the latest semiconductor-device technique in the active matrix circuit of a solar battery or a liquid crystal display with the orientation of detailed-izing represented by semiconductor memory and image sensors and integration. In a large area semiconductor device, it is necessary to lower the manufacturing cost per unit area as much as possible. Therefore, the semiconductor thin film of amorphous ***** deposited on cheap substrates, such as glass, a metal, and a ceramics, with the single crystal silicon wafer as a semiconductor material is beginning to use. However, in order to lower the manufacturing cost of a device, low-cost-ization is demanded about each of other manufacture process. Moreover, the manufactured device must have a uniform property over 30cm angle or the large area beyond it. That is, suitable process technique must be developed by it at a large area device.

[0003] Doping technique is mentioned as most important technique from the viewpoint of large-area-izing also in each manufacture process.

[0004] Most generally as doping technique of a semiconductor, the thermal diffusion method has been used. A thermal diffusion method is technique which usually diffuses in a semiconductor the dopant atom contained in the layer applied or deposited on the semiconductor from face at the elevated temperature of 1000 degrees C or more, and is activated as a dopant. Although this technique can be applied to a large area device comparatively easily, in order to use an elevated temperature, it faces using a thin film semiconductor and a constraint is received in an usable substrate. Moreover, processing takes a long time (usually several about hours), and the throughput of a manufacture is not good.

[0005] Moreover, there is the ion implantation method as other general doping techniques. It is the technique of accelerating by the electric field, devoting itself into a semiconductor, usually annealing about several hours at the temperature of 800 degrees C or more, and activating a dopant from the beam of the dopant atom ion ionized in the vacuum by this technique, after removing an impurity by the means of a mass analysis. Although it is easy to carry out a control of a dopant by this technique, it is necessary to scan a beam over a large area, and the throughput of a manufacture is not good too. Moreover, equipment becomes large-scale and becomes too disadvantageous in respect of a cost.

[0006] On the other hand, in the case of the thin film semiconductor deposited from a gaseous phase by technique, such as heat CVD and plasma CVD, there is the technique of mixing the gas which contains a dopant in a gaseous phase at the time of deposition of a thin film, and introducing a dopant atom into a thin film semiconductor. The property of the semiconductor of n type formed by this technique although it was good for large-area-izing to also have been comparatively easy, and to also have compared a throughput with a thermal diffusion method or the ion implantation method, or p type was not necessarily enough, and the application to a semiconductor device had many inadequate things. It becomes what was inferior compared with the case where the crystal grain of Si will especially become small by high concentration if a phosphorated hydrogen (PH₃) tends to be mixed to the mono silane (SiH₄) of a raw material in case polycrystal Si is deposited with heat CVD as an example known well, and it is going to make it n type, and the property as n type Si makes it n type by the thermal-diffusion-method and ion in plastic ***** method. Moreover, in case an amorphous silicon (a-Si) is deposited by the plasma CVD method, it is SiH₄ of a raw material. If a diboron hexahydride (B₂H₆) tends to be mixed and it is going to make it p type, an optical band gap (E_g) falls, a localized level will increase and the property as a p type semiconductor will become what was inferior.

[0007] If the gas containing a dopant is mixed in a gaseous phase as the ground, the reaction of the gas containing the elements (Si etc.) of the principal component which constitutes a semiconductor will be affected, and it will be considered for changing the precursor (precursor of a deposition reaction) of deposition of a semiconductor.

[0008] Moreover, if it dopes by deposition, generally the semiconductor field of n type or p type cannot be alternately formed in the specific location on a substrate. For this reason, a process is complicated especially in the application to a liquid crystal display. Some proposals are made from such a viewpoint.

[0009] M. B. Spritzer and S. N. Brunker The ion implantation of ** 1 μm (P) which does not perform a mass analysis to p type single crystal Si was performed, and the solar battery of 15% of the conversion efficiencies with pn junction was made (16th IEEE Photovoltaic Conf. San Diego and 1982p 711-). H. Itoh etc. made the solar battery of 10% of

conversion efficiencies without the acid-resisting layer by the same technique (Proc. 3rd PV/Si:C in Japan (82) p. 7-). By the ion in plastic ***** method do not perform a mass analysis, equipment becomes comparatively easy and its throughput of a manufacture also improves. However, in applying to a solar battery, processing of the large area of sufficient like is difficult. Moreover, after driving in ion in their experiment, the annealing is performed above 550 degrees C or 600 degrees C, and there are many constraints to the application to the throughput of a manufacture being not only low but a thin film semiconductor.

[0010] Moreover, S.J.D. Westbrook etc decomposes the gas containing boron (B) by glow discharge, after accelerating boron ion and devoting oneself to n type single crystal Si by impressing the electric field further, performs annealing above 550 degrees C, and is making the solar battery of no less than 19% of conversion efficiencies (Appl Phys Lett Vol. 50 (87) p. 469-). On the other hand, Yoshida, Setsume, and Hirao perform doping to a-Si of 1 μ m using the same equipment, and are making the thin film transistor (TFT) (JEE Device Lett Vol. 9 (1988) p. 90-). By such technique, it is easy to carry out large area-ization, and the throughput of a manufacture is also comparatively good. Moreover, a p type or n type field can be alternatively formed in the specific location of a semiconductor side as the latter is shown. However, in order not to perform a mass analysis, various kinds of unnecessary ion will also be driven in at high speed in addition to dopant ion. Therefore, especially when annealing at sufficient temperature was difficult a-Si, it was hard to remove the damage by ion, and it had become the failure which gets poisoned by the application to an a-Si solar battery. Moreover, about a neutral dopant atom except ion, a control is impossible, and it is easy to diffuse these dopant atoms to each part of equipment. Especially, in the a-Si solar battery, the pin junction is usually used, and it consists of six layers and nine layers from three n type, 1 type, and p type layers at least in the tandem-die a-Si cell which carried out the laminating of further two or more pin junctions. These dopants will tend to have a bad influence on the property of a device, if it mixes in the semiconductor layer (especially 1 layers) from which an adjoining conductivity type is different. With the roll-to-roll equipment which performs continuity deposition to a long band-like substrate for the purpose of the mass production of an a-Si solar battery especially, a diffusion of the dopant to an adjoining membrane formation room tends to happen.

[0011] Thus, in order to mass-produce a highly efficient a-Si solar battery, the doping technique to a large area needs to be improved further. Moreover, also in the case of the crystal semiconductor solar battery and the liquid crystal display, the development of the good doping technique of the throughput of a manufacture was desired.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] It is making to form the field of the semiconductor of p type with a good property, or n type by irradiating a ultraviolet radiation on the surface of a semiconductor, and activating a dopant in the operation, in case this invention deposits a dopant layer by the sputtering method on the surface of a semiconductor into main point.

[0014] That is, making a dopant deposit on the surface of a semiconductor by the sputtering method using the target containing a dopant element, it makes the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least act on the front face of the aforementioned semiconductor, and the doping technique of the semiconductor of this invention dopes to the aforementioned semiconductor.

[0015] Moreover, after the doping technique of the semiconductor of this invention deposits a dopant on this front face by the sputtering method using the target containing a dopant element, it makes the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least act on this front face, and dopes to the aforementioned semiconductor.

[0016] The doping system of the semiconductor of this invention is equipped with the chamber in which the evacuation with which a semiconductor is set is possible on the other hand, the anode prepared in the interior of the aforementioned chamber, the cathode with which the target containing a dopant element was set to the front face, the power which supplies power to this cathode, the light source which irradiates the ultraviolet radiation which contains a component with a wavelength of 300nm or less at least on the front face of the aforementioned semiconductor, and the line for supplying inert gas to the aforementioned chamber at least.

[0017] Furthermore, the doping system of the semiconductor of this invention should be equipped with a means to convey a semiconductor, between the positions which counter the light source which irradiates the position which counters a target, and a ultraviolet radiation.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention is made in view of such present condition, and an unnecessary diffusion of a dopant is easy few equipment in a manufacture of a semiconductor device. In the semiconductor of p type which was excellent in the property, or n type, homogeneity is good over a large area. The equipment for enforcing the technique of manufacturing by the short processing time and this technique is offered, and especially, the manufacture by the low cost of the semiconductor device of a large area like a highly efficient solar battery or a liquid crystal display is enabled, and it aims at contributing to the spread of these devices.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1 This document has been translated by computer. So the translation may not reflect the original precisely.
- 2 **** shows the word which can not be translated.
- 3 In the drawings, any words are not translated.

Effect

[Effect of the Invention] According to the doping technique of this invention, and equipment, it can dope, without doing big trauma to the parent of a good semiconductor, and since the after treatment in an elevated temperature is unnecessary, it can be amorphous, and **** cannot be asked but a single crystal, polycrystal, p type that was excellent in the property, or an n type semiconductor field can be formed to various kinds of semiconductors. And since there is no unnecessary diffusion of a dopant, the semiconductor device which was excellent in the property can be obtained. Moreover, the configuration of equipment is easy, a uniform property is acquired over a large area, and since the processing time is short, a large-sized solar battery, the active matrix circuit of a liquid crystal display, etc. can be especially manufactured in a low cost.

[Translation done]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
 2. **** shows the word which can not be translated
 3. In the drawings, any words are not translated.

OPERATION

[1]unction] Drawing 1 is an outline block diagram showing the embodiment of the doping system of a suitable this invention to enforce the doping technique of this invention.
 [0019] In the chamber 101 in which evacuation is possible, one pair of electrodes of the anode 103 and the cathode 104 are prepared by the vacuum pump 102. The sample 105 is set to the anode 103.

[0020] The polycrystal and the amorphous semiconductor thin film which were deposited on substrates, such as a semiconductor wafer of a single crystal or a polycrystal and a glass metallurgy group, as a sample are used. These semiconductors may be beforehand doped according to the purpose, and do not need to be doped. A sample 105 can be heated to desired temperature at a heater 106. The cathode 104 is connected to the power 108 for occurring a plasma 107 between an anode 103 and the cathode 104. The target 109 is set on the cathode 104. As a material of a target, B, aluminum, Ga, In, Tl, P, As, Sb, Bi, etc. are used. A RF generator is sufficient although DC power supply are sufficient as power 108, especially -- a target material -- high -- when ****, the power of radio frequencies, such as 13.56 etc MHz, can use it suitably. Inert gas, such as Ar, is introduced into a chamber 101 from a bomb 110. The flow rate of inert gas is adjusted by the mass-flow controller 111. And the pressure in a chamber 101 is adjusted by the opening of the mass-flow controller 111 and the butterfly valve 114. Moreover, in the chamber 101, the mercury-vapor lamp 112, 113 (it is henceforth described as the light source 112, 113) is further formed as light source of a ultraviolet radiation, and the front face of a sample 105 can be irradiated now at any time.

[0021] The following experiments were conducted in order to check a one experiment effect of the invention. p type Si wafer (1 ohm of specific resistances, cm) which carried out the sintering of the golden electrode to the rear face was made into the sample 105, and it set to the doping system of drawing 1. (Once exhausting the inside of a chamber 101 to 10⁻⁶ Torr. Ar was passed 5 secms, the butterfly valve 114 was adjusted, and the pressure was set to 10⁻³ Torr. Subsequently, the current of a heater 106 was adjusted so that substrate temperature might become 100 degrees C. As a target 109, the plate of the simple substance of P of 99.99% of purity was used. Subsequently, the light source 112, 113 was turned on. When the RF power of 200W was supplied, adjusting a non-illustrated matching circuit so that reflective power may serve as the minimum from power 108 in this status, the plasma 107 occurred. Supply of the power to power 108, the light source 112, 113, and the heater 106 was stopped in the place which passed for 100 seconds in this status. After the sample cooled, it took out from the inside of a chamber 101, started on 1cm square, and was referred to as sample 1A.

[0022] Next, the light source 112, 113 was not turned on for the comparison, and also sample 1B was made from the completely same process as the above.
 [0023] Next, lead wire was fixed with a silver paste on the rear face and front face of samples 1A and 1B. The volt-ampere characteristic of both samples in the dark was measured first. At sample 1A, the rectification ratio in 1V is 3x10⁴. It was twice. By sample 1B, the rectification ratio was able to be taken only 50 times to it. Furthermore, the solar-battery property of both the samples in the basis of the solar simulator of the air mass (AM) 1.5 was seen. In sample 1A, the property good as a solar battery, that 9.3% and an antireflection film do not have a conversion efficiency (eta) was acquired. On the other hand, sample 1B of the conversion efficiency (eta) was [the function as 2.7% and a solar battery] inadequate.

[0024] Except not turning on the light source 112, 113 by experiment 2 view 1, after the same procedure as experiment 1 performed sputtering, the light source 112, 113 was turned on for 10 minutes, and sample 2A was made. Moreover, the light source 112, 113 was not turned on, but sputtering was performed for 50 seconds, subsequently
 ***** during 5 minutes was irradiated, sputtering and ultraviolet-radiation irradiation were repeated on the again same conditions, and sample 2B was made.

[0025] The rectification ratio of 1V in the dark is 2x10³ at sample 2A. In twice and sample 2B, it was 1x10⁵ times. Moreover, the conversion efficiency (eta) of sample 2A was [the conversion efficiency (eta) of sample 2B of the solar-battery property in AM1.5] 8.9% 7.8%.

[0026] Since it was shown that experiment 3 this invention is effective also to an amorphous semiconductor, a solar battery which is shown in view 2 was made. commercial RF capacity-coupling type glow discharge equipment -- the stainless substrate 201 with a thickness of 1mm -- setting -- a this top -- the n-type-semiconductor layer 202 of a-Si -- subsequently the p-type-semiconductor layer 203 of a-Si was deposited. The creation conditions of the n-type-semiconductor layer 202 are 5% of P113 as material gas. Mixed

SnH₄ It carries out in 5secs, pressure 0.5 Torr, electric discharge power 50W, and substrate temperature of 250 degrees C, and a thickness is 2000*. The creation conditions of the i-type-semiconductor layer 203 are SnH₄ as material gas. It carries out in 20secs, pressure 0.5 Torr, electric discharge power 100W, and substrate temperature of 250 degrees C, and a thickness is 4000*. In this way, the sample was set to the equipment of drawing 1. The plate of the simple substance of B of 99.9% of purity was used as a target 109.

[0027] Having been referred to as Ar5secm, pressure 10-3 Torr, the substrate temperature of 200 degrees C, and electric discharge power 200W, and turning on the light source 112, 113 as doping conditions, electric discharge was continued for 50 seconds and p type field 204 was created.

[0028] After the sample cooled, it took out from the chamber 101, and it set to the commercial resistance heating type vacuum evaporation system, the vacuum evaporation of the alloy of In and Sn was carried out in the oxygen ambient atmosphere, the thickness 7000* deposition of the transparent electrode 205 of TlO (In₂O₃+SnO₂) layer was done, and it was referred to as sample 3A. The sample which used the n-type-semiconductor layer 202 as the p type a-Si layer of thickness 2000* in drawing 2 was set to the doping system of drawing 1, and the p type field 204 was formed on the same doping conditions as the above using the target of P. The transparent electrode 205 was formed similarly and it was referred to as sample 3B.

[0029] The same procedure as experiment 1 estimated both the samples 3A and 3B. For the rectification ratio of 1V, sample 3A is 1x10⁵. Twice and sample 3B are 8x10⁴. It was twice. Moreover, 8.5%, sample 3A is 7.8% and, as for the conversion efficiency (eta) as a solar battery, sample 3B showed the property excellent in all.

[0030] Based on the above experimental result [device / of doping], it can guess as follows about the device of the method of doping this invention. In the sputtering method, although ion, such as Ar, exists in the plasma of electric discharge, these ion strikes the target 109 on the cathode 104 by which the bias is carried out to negative. The configuration atom of the target which recoils as a result accumulates on a sample 105. Generally a dopant atom will seldom invade to the interior of a sample, since it is neutral and it is not accelerated by the electric field, however, since it is combinable by the suitable coordination number finally [invade and] until the atom of a sample of a dopant is deep, in order to loosen a combination of Si which constitutes a semiconductor mutual [atomic] by the energy of the photon of a ultraviolet radiation, if a ultraviolet radiation is irradiated by the sample side, it is thought that it is activated as a dopant.

[0031] Therefore, since there is no damage like [at the time of driving in the ion with which a thermal diffusion called 100 degrees C] was accelerated at high speed / can perform effective doping and / also in the low temperature which is not expectable at all], it is thought that the annealing as after treatment also becomes unnecessary.

[0032] Moreover, in heat CVD or a plasma CVD method, since the network of the parent of a semiconductor is formed without the bad influence of a dopant by the technique of this invention unlike the case where a semiconductor accumulates in the ambient atmosphere containing a dopant, it is expectable that formed p type layer and n type layer show the outstanding property.

[0033] Furthermore, in the case of the sputtering method, since a dopant atom starts skipping with a remarkable directivity toward a sample from a target, it is expectable that a diffusion of the dopant to the unnecessary location decreases sharply as gas compared with the case where a dopant is supplied.

[0034] The simple substance of a desired dopant element can be used as a material of the target used in enforcing the technique of this invention about a target. Namely, what is necessary is just to use the simple substance or alloy of P, As, Sb, and Bi with 4 group semiconductors, such as Si and germanium, in order to consider as p type and to use the simple substance or alloy of B, aluminum, Ga, In, and Tl as n type. Although the purity of these materials has the good higher one, generally at least its about 99% is usable by the modality of impurity 99.9%. Moreover, although it is easy to use a plate-like thing as a configuration of a target, when the thing which pressed the powdered material, and a cathode are facing up, it is even good to have piled powder on the cathode.

[0035] Most generally Ar is used as a controlled atmosphere by the sputtering method about the controlled atmosphere of sputtering. Ar of an ionization rate is high and this is for hammering out a target atom most efficiently. However, for the purpose of doping, a not much big rate of sedimentation has that it is [much] unnecessary, and can also use inert gas, such as helium, Ne, Kr, and Xe, in addition to Ar.

[0036] The technique of this invention is applicable about doping conditions also not only to the semiconductor of four groups, such as Si, and germanium, its alloy, SiC, but compound semiconductors, such as GaAs and InP. However, a dopant is suitably chosen from the element of two groups, four groups, and six groups according to the semiconductor of a parent. The flow rate of inert gas, such as Ar, is suitably decided as gas of the ambient atmosphere of electric discharge according to a sample size. The pressure at the time of electric discharge is preferably set to 5x10⁻⁴ Torr to 0.1 Torr 0.5 Torr from 1x10⁻⁴. Although electric discharge power is also decided according to a sample size, when it is the sample of 30cm angle, 5kW is preferably set to about 250W to 2kW from 100W. Although a good result may be obtained at a room temperature as substrate temperature, generally you may be 60 degrees C or more. In almost all cases, effect sufficient at about 200 degrees C is acquired.

[0037] As light used for irradiation about the irradiation technique of a ultraviolet radiation, the ultraviolet radiation with a wavelength of 250nm or less is still preferably effective. 150nm or more 300nm or less wavelength. As light source, a commercial mercury-vapor lamp is used suitably. However, in air, since the light of such a wavelength field receives absorption and generates ozone, preparing into a vacuum chamber is desirable [the light source] like the doping system of drawing 1.

[0038] In the case of the doping system of drawing 1, since the light source 112, 113 is formed near the target 109, if it is used over a long time, dirt will adhere

[0039] Moreover, it is difficult to irradiate a ultraviolet radiation uniformly over the whole sample from face of a large area with this configuration. [0040] However, it prepares in the position which is distant from a cathode 304 in the light source 312 in the large-sized chamber 301 as it was shown in drawing 3, since it was effective even if it performs irradiation of a ultraviolet radiation after deposition of a dopant, as the experiment 2 was shown, an anode 303 is moved to the position of after sputtering and the light source 313, and it may be made to irradiate a ultraviolet radiation.

[0041] drawing -- three -- setting -- a vacuum pump -- 302 -- an anode -- 303 -- a cathode -- 304 -- a sample -- 305 -- a heater -- 306 -- power -- 308 -- a target -- 309 -- a bomb -- 310 -- a mass flow -- a controller -- 311 -- and -- a butterfly valve -- 314 -- respectively -- drawing -- one -- being shown -- a vacuum pump -- 102 -- an anode -- 103 -- a cathode -- 104 -- a sample -- 105 -- a heater -- 106 -- power -- 108 -- a target In especially large-sized equipment, the configuration of drawing 3 is easier for the design. Moreover, it is better to seldom have continued sputtering at once for a long time but to repeat this move two or more times to thicken a dope layer.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE 1:

[Example] Although the semiconductor surface treatment technique of this invention and the example of equipment are described below and this invention is further explained to it, thereby, this invention is not limited at all.

[0043] In example 1 this example, the pin type a-Si photovoltaic cell 408 of the lamination shown in the cross section of drawing 4 was produced using the equipment shown in drawing 1. This photovoltaic cell 408 is a photovoltaic cell which carried out deposition formation of the lower electrode 402, the n-type-semiconductor layer 403, the i-type-semiconductor layer 404, the p type semiconductor layer 405, the transparent electrode 406, and the current collection electrode 407 on the substrate 401 at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 406 side in the photovoltaic cell 408 of this example.

[0044] First, the sputtering system (the UJ VAC Corp. make, SBH-2206D1) of marketing of the square shape substrate made from stainless steel (5cmx5cm) -- setting -- Ag (99.99%) -- target ***** -- using -- 0.3-micrometer Ag thin film -- moreover, the sputter vacuum evaporation of the 1.5-micrometer ZnO thin film was carried out continuously, using Zn (99.9%) as a target, and the lower electrode 402 was formed.

[0045] Then, the substrate in which this lower electrode 402 was formed was set to commercial plasma CVD equipment (the IJ VAC Corp. make, CHJ-3030). The exhaust air pump performed a skimming and high-vacuum length operation through the exhaust pipe of a reaction container. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[0046] When exhaust air was fully performed, from the gas introduction spool, SiH₄ 300sccm, SiF₄ 4sccm, PH₃ / H₂ 55(1% H₂ dilution) sccm, and H₂ 40sccm were introduced, the opening of a throttle valve was adjusted, the internal pressure of a reaction container was held to 1 Torr, and the power of 200W was immediately switched on from the RF generator in the place by which the pressure was stabilized. The plasma was made to maintain for 5 minutes. Thereby, it is n+ The n+a-Si:H F layer as a semiconductor layer 403 was formed on the lower electrode 402.

[0047] Immediately after exhausting again, SiH₄ 300sccm, SiF₄ 4sccm, and H₂ 40sccm were introduced from the gas introduction spool, the opening of a throttle valve was adjusted, the internal pressure of a reaction container was held to 1 Torr, and the power of 150W was switched on from the RF generator in the place by which the pressure was stabilized, this time. The plasma was made to maintain for 40 minutes. Thereby, the a-Si:H F layer as a i-type-semiconductor layer 404 was formed on the n-type-semiconductor layer 403.

[0048] Next, the substrate 401 was taken out from plasma CVD equipment, and it set to the doping system shown in drawing 1. Boron (B) is used as a target, electric discharge is continued for 70 seconds, irradiating a ultraviolet radiation on condition that Ar flow rate 5sccm, pressure 2x10⁻³Torr, the substrate temperature of 100 degrees C, and electric discharge power 200W, and the p type semiconductor layer 405 was formed on the i-type-semiconductor layer 404.

[0049] Next, the transparent electrode 406 (ITO (In₂O₃+SnO₂)) was formed with vacuum deposition, the mask vacuum evaporation of the current collection electrode 407 (aluminum) was carried out further, and the photovoltaic cell 408 was completed.

[0050] About the produced photovoltaic cell 408, when the characterization was performed under air mass (it is henceforth described as AM) 1.5 (100mW/cm²) light irradiation, 9.3% was obtained by the photoelectric conversion efficiency (eta). Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm²) light was measured, it ***** to less than 20%.

[0051] In example 2 this example, a-Si / a-Si tandem-die photovoltaic cell 613 of the lamination shown in the cross section of drawing 6 were produced using the roll-to-roll equipment 512 shown in drawing 5.

[0052] This photovoltaic cell 613 is the n-type-semiconductor layer 603 which constitutes the lower electrode 602 and the 1st cell 611 on a substrate 601, the i-type-semiconductor layer 604, the p type semiconductor layer 605, the n-type-semiconductor layer 606 that constitutes the 2nd cell 612 further, the i-type-semiconductor layer

607, the p type semiconductor layer 608, and a photovoltaic cell that carried out deposition formation of the transparent electrode 609 and the current collection electrode 610 further at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 609 side in the photovoltaic cell 613 of this example.

[0053] The roll-to-roll equipment 542 of drawing 5 forms a photovoltaic cell in the band-like substrate 504 made from stainless steel continuously. As for the equipment of this drawing, the substrate send room 503, 1st n type chamber 513, 1st i type chamber 522, 1st p type chamber 532, 2nd n type chamber (un-illustrating), 2nd i type chamber (un-illustrating), 2nd p type chamber (un-illustrating), and the substrate rolling-up room 539 are arranged at this order. 2nd n type chamber, 2nd i type chamber, and 2nd p type chamber are the completely same respectively configurations as 1st n type chamber 513, 1st i type chamber 522, and 1st p type chamber 532, between each chamber, it is isolated by the gas gates 507 and 515, 524, 533, 536 (others -- un-illustrating), and mixing of the impurity between chambers is prevented.

[0054] In this drawing, first, the substrate send room 503 is ** to which the band-like substrate 504 is set, and a substrate is continuously taken out through a guide roller 505 from this **. during membrane formation to a reaction chamber. Moreover, evacuation is carried out through the exhaust port 502 and the bulb 501. The substrate rolling-up room 539 is ** by which the formed band-like substrate 538 is rolled round, and a substrate is continuously carried in to this ** from a reaction chamber through a guide roller 537 during membrane formation. Moreover, evacuation is carried out through the exhaust port 540 and the bulb 541.

[0055] n type chamber 513 and i type chamber 522 are plasma (CVI) chambers, and deposit a n-type-semiconductor layer and a i-type-semiconductor layer, respectively. A substrate is heated at the substrate heating heater 514, 523 within each chamber 513, 522, and it is controlled by predetermined substrate temperature. It is supplied from the material gas supply pipe 510, 518, and flowing is prepared with the shield plate 512, 521, it is decomposed by the plasma which occurred between the cathode 511, 520 and the substrate, a semiconductor layer is formed on a substrate, and material gas is further exhausted from an exhaust port 509, 519.

[0056] p type chamber 532 is the embodiment of the doping system of this invention which used the technique of this invention. A substrate is controlled by the substrate heating heater 531 by predetermined temperature. Evacuation of the inside of a chamber is carried out from an exhaust port 528. The target 530 of boron (B) is set to the front face of a cathode 529. With this roll-to-roll equipment 542, a substrate functions as an anode and a plasma occurs between cathodes 529. After the light source 530 of a ultraviolet radiation is formed beside a cathode and a dopant deposits it on a i-type-semiconductor layer first in connection with a move of a substrate, a ultraviolet radiation is irradiated and a dopant activates it. By this configuration, the continuous duty of the ultraviolet light source covering a long time becomes possible. Ar is supplied from the material gas supply pipe 527.

[0057] in order to isolate the gas between chambers, sweep gas, such as Ar and hydrogen, is introduced into the gas gates 507 and 515, 524, 533, 536 (others -- un-illustrating) from gas inlets 506, 508, 516, 517, and 525, 526, 534, 535 (others -- un-illustrating).

[0058] The photovoltaic cell 613 was produced using such roll-to-roll equipment 542.

[0059] first, the band-like substrate made from stainless steel -- a continuity sputtering system (un-illustrating) -- setting -- aluminum-Si (5%Si) -- target ***** -- using -- a 0.2-micrometer aluminum-Si thin film -- moreover -- continuing -- SnO₂ (99.99%) -- target ***** -- using -- 0.1-micrometer SnO₂. The sputter vacuum evaporations of the thin film was carried out, and the lower electrode 602 was formed.

[0060] Then, it set to the roll-to-roll equipment 542 in which the band-like substrate in which this lower electrode 602 was formed was shown in drawing 5. Then, the exhaust air pump (un-illustrating) performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[0061] When exhaust air was fully performed, in n type chamber, it is SiH₄ / PH₃ / H₂ from the gas introduction spool 510, 518. In i type chamber, it is SiH₄ / SiF₄ / H₂. Ar gas was introduced into p type chamber and the gas gate, and the pressure of p type chamber held again the internal pressure of n type and i type chamber to 100mTorr at 50mTorr.

[0062] In the place by which the pressure was stabilized, switched on power from each RF generator, and made the plasma occur within each chamber, and turned on the light source, the band-like substrate was made to convey in the orientation of right-hand side from the left-hand side in drawing by conveyance speed 20cm/min in the place by which electric discharge etc. was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[0063] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, it took out after cooling, and it set to ITO (In₂O₃+SnO₂) continuity vacuum evaporations equipment (un-illustrating), the vacuum evaporations of the ITI layer of thickness 700** was carried out covering the band-like substrate overall length, and it considered as the transparent electrode 609. Furthermore, continuity production of the 35cmx70cm solar-battery module was carried out with continuity modularization equipment (un-illustrating).

[0064] About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm²) light irradiation, 8.0% or more is obtained by the photoelectric conversion efficiency (eta), and the variation in the property between modules had *****ed to less than 7% further.

[0065] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm²) light was measured, it *****ed to less than 16%.

[00066] These modules were able to be connected and the 1kW electric power supply system was able to be produced

[00067] When the photovoltaic cell same without passing sweep gas to each gas ***** because of a comparison was created, 7.8% or more of photoelectric conversion efficiencies (η) is obtained, and the rate of a degradation of 500 hours after had ***** to less than 18%. That is, it was slight although the influence of a diffusion of the dopant between each chamber accepted a little even if it did not use sweep gas

[00068] In example 3 this example, the roll-to-roll equipment 542 to which a-Si/a-Si tandem-die photovoltaic cell of the lamination shown in the cross section of drawing 6 like an example 2 are shown in drawing 5 was produced using the equipment (un-illustrating) converted in part Having used the doping system of the 1st or 2nd p type chamber and the same this invention of ** for 2nd n type chamber differs from the equipment of drawing 5.

[00069] The target of boron (B) is used for the 1st and 2nd p type chambers, and the target of antimony (Sb) is used for 2nd n type chamber.

[00070] The photovoltaic cell 613 was produced using such roll-to-roll equipment.

[00071] first, the example 2 -- the same -- the band-like substrate made from stainless steel -- a continuity sputtering system -- setting -- aluminum-Si (5%Si) -- target ***** -- using -- a 0.5-micrometer aluminum-Si thin film -- moreover, the sputter vacuum evaporation of the 0.5-micrometer ZnO thin film was carried out continuously, using ZnO (99.99%) as a target, and the lower electrode 602 was formed

[00072] Then, the band-like substrate in which this lower electrode 602 was formed was set to the roll-to-roll equipment of this example. Then, the exhaust air pump performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[00073] the time of exhaust air fully being performed -- a gas introduction spool -- 1st n type chamber -- SiH4 / PH3 / H2 In the 1st and 2nd i type chambers, it is SiH4 / SiF4 / H2. Introduce Ar gas into the 1st and 2nd p type chamber and 2nd n type chamber, and the gas gate, and the opening of a throttle valve is adjusted. The pressure of 2nd n type chamber and the 1st, and 2nd p type chamber held again the internal pressure of 1st n type and the 1st, and 2nd i type chamber to 100mTorr at 50mTorr. In the place by which the pressure was stabilized, the light source of a each p type chamber was turned on, from each RF generator, switch on power, made the plasma occur within each chamber, the band-like substrate was made to convey by conveyance speed 20cm/min in the place by which electric discharge etc. was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[00074] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, further, it took out after cooling, and the vacuum evaporation of the TiO (In2O3+SnO2) layer was carried out, the transparent electrode 609 was formed and continuity production of the 30cmx120cm solar-battery module was carried out with continuity modularization equipment. About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm2) light irradiation, 8.5% or more is obtained by the photoelectric conversion efficiency (η), and the variation in the property between modules had ***** to less than 10% further.

[00075] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm2) light was measured, it ***** to less than 15%.

[00076] In example 4 this example, the roll-to-roll equipment 542 to which the a-SiC/a-Si/a-SiGe triple mold photovoltaic cell of the lamination shown in the cross section of drawing 7 is shown in drawing 5 was produced using the equipment (un-illustrating) converted in part. The equipment adds the 3rd n type, i type, and p type chamber to the equipment used in the example 2 further, and only the 1st to 3rd p type chamber of the doping chamber of this invention and other chambers is a plasma CVD chamber.

[00077] The photovoltaic cell 717 shown in drawing 7 using such roll-to-roll equipment was produced.

[00078] This photovoltaic cell 717 (On a substrate 701, the lower electrode 702 and the 1st cell 714. The n-type-semiconductor layer 703 to constitute, the i-type-semiconductor layer 704, the p type semiconductor layer 705, the n-type-semiconductor layer 706 that constitutes the 2nd cell 715 further, the i-type-semiconductor layer 707, the p type semiconductor layer 708, the n-type-semiconductor layer 709 that constitutes the 3rd cell 716 further, the i-type-semiconductor layer 710. They are the p type semiconductor layer 711 and the photovoltaic cell which carried out deposition formation of the transparent electrode 712 and the current collection electrode 713 further at this order. In addition, it is premised on incidence of light being performed from a transparent-electrode 712 side in the photovoltaic cell 717 of this example

[00079] first, the example 2 -- the same -- the band-like substrate made from stainless steel -- a continuity sputtering system -- setting -- aluminum (99.99%) -- target ***** -- using -- 0.3-micrometer aluminum thin film -- moreover, the sputter vacuum evaporation of the 0.3-micrometer ZnO thin film was carried out continuously, using ZnO (99.99%) as a target, and the lower electrode 702 was formed

[00080] Then, the band-like substrate in which this lower electrode 702 was formed was set to roll-to-roll equipment. Then, the exhaust air pump performed vacuum length operation through the exhaust pipe of each chamber. At this time, the skin temperature of a substrate was controlled by the temperature-control device to become 250 degrees C.

[00081] the time of exhaust air fully being performed -- a gas introduction spool -- a each n type chamber -- SiH4 / PH3 / H2 1st i type chamber -- SiH4 / SiF4 / H2 2nd i type

chamber -- SiH₄ / SiF₄ / I₂ In 3rd i type chamber, it is SiH₄ / ClH₄/I₂. Moreover, introduce Ar gas into a each p type chamber and the gas gate, and the opening of a throttle valve is adjusted. The pressure of a each p type chamber held again the internal pressure of every n type and a each i type chamber to 100mTorr at 50mTorr.

[00082] In the place by which the pressure was stabilized, the light source of a each p type chamber was turned on, from each RF generator, switch on power, made the plasma occur within each chamber, the band-like substrate was made to convey by conveyance speed 30cm/min in the place by which electric discharge was stabilized, and laminating formation of n, i, p, n, i, and the p type semiconductor layer was carried out continuously.

[00083] After carrying out laminating formation of the semiconductor layer covering the overall length of a band-like substrate, it took out after cooling, and the vacuum evaporation of the ITO (In₂O₃+SnO₂) layer was carried out, the transparent electrode 609 was formed and continuity production of the 30cmx120cm solar-battery module was further carried out with continuity modularization equipment.

[00084] About the produced solar-battery module, when the characterization was performed under AM1.5 (100mW/cm²) light irradiation, 10.2% or more is obtained by the photoelectric conversion efficiency (η), and the variation in the property between modules had ****ed to less than 5% further.

[00085] Moreover, when the rate of change to the initial value of the photoelectric conversion efficiency after the 500 hour continuous irradiation of AM1.5 (100mW/cm²) light was measured, it ****ed to less than 8%.

[00086] These modules were able to be connected and the 5kW electric power supply system was able to be produced.

[00087] The polycrystal Si solar battery 801 of a configuration as example 5 this example is shown in drawing 8 is explained. The n type polycrystal Si wafer (2 ohms of specific resistances, cm) with which the front face made from Wacker was ground and which is the diameter of 6 inches was prepared as a substrate. After removing a natural-oxidation layer in fluorine acid, this substrate was set so that a polished surface might become a large-sized doping system with public although it was the same structure as the doping system of drawing 1. The plate of Ga of 99.99% of purity was used as a target 109. As doping conditions, Ar flow rate 20scm, pressure 10-3Torr, substrate temperature of 100 degrees C, and electric discharge power were set to 1kW, continued irradiation of a ultraviolet radiation, and electric discharge for 150 seconds, and formed p type field 802.

Subsequently, it is n+ at the same doping conditions except exchanging a target 109 for the plate of Sb of 99.99% of purity, and having reset the substrate inside out. The type field 803 was formed. This n+ The type field 803 is for forming the so-called back surface field, preventing the recombination near the electrode of a carrier, and raising ohmic nature further. Subsequently, the current collection electrode 804 and the lower electrode 805 which become both sides from the laminating of Ti, Pd, and Ag were formed by the electron-beam-evaporation method. The surface electrode covered the mask and made it the shape of a grid so that the incidence of light might seldom be barred. After forming an electrode, the sintering was performed for 2 minutes at 400 degrees C. Subsequently, it is ZnS and MgF₂ to a front face. The laminating was carried out and it considered as the acid-resisting layer 806.

[00088] When this sample was cut on 2cm square and the solar-battery property was evaluated, the property and homogeneity in which the photoelectric conversion efficiency (η) was extremely excellent with 15.24**0.61% were acquired.

[00089] Example 6 this example is an example of the a-Si thin film transistor (TFT) which shows the cross-section structure in drawing 9. (Forming #7059 glass was used as the substrate 901, on this, the vacuum evaporation of the Cr was carried out and the gate 902 was further formed at the photo-lithography process. Subsequently, it is SiH₄ by commercial capacity-coupling type RF glow discharge equipment. The amorphous silicon-nitride (a-SiN) layer 903 of thickness 3000** was deposited for ammonia (NH₃) as material gas. The i type a-Si layer 904 of thickness 2000** was deposited using the equipment same besides. The a-SiN layer of thickness 3000** was again deposited with the equipment same besides, and it left the channel 905, and etched at the photo-lithography process. It sets to the same doping system as what used the sample in the example 5 after this, and flow rate 30scm of Ar, pressure 5x10-3Torr, and the substrate temperature of 80 degrees C are continued as doping conditions, irradiation of a ultraviolet radiation and electric discharge are continued for 200 seconds as electric discharge power 800W, using the plate of P of 99.99% of purity as a target, and it is n+. The type field 906 was formed. Since a-SiN of a channel 905 is an insulator, the low resistance field by doping is not made on a front face by it here. Subsequently, on this, aluminum was carried out thickness 2000** vacuum evaporation, the channel 905 was further etched at the photo-lithography process, and TFT was formed as the source 907 and a drain 908. In addition, channel length is 10 micrometers here. Thus, lead wire was respectively fixed in the gate 902 of manufactured TFT, the source 907, and the drain 908, and transistor characteristics were evaluated over the domain of 20cm angle (ON/OFF ratio with gate voltages 15V and 0V is 1.5x10⁵ at the time of drain voltage 15V. It excelled with twice**89%. By the technique of this invention, in order that the channel section may be protected by a-SiN and may not receive processing of etching etc., (ON/OFF ratio is greatly considered that homogeneity is also excellent. Therefore, it is the best for using TFT by the technique of this invention for the active matrix circuit of a large-sized liquid crystal display.

[Translation done]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing the embodiment of the doping system of a suitable this invention to enforce the doping technique of this invention.

[Drawing 2] It is the ***** type view showing the a-Si solar battery created by the doping technique of this invention.

[Drawing 3] It is the outline block diagram showing another embodiment of the doping system of a suitable this invention to enforce the doping technique of this invention.

[Drawing 4] It is the ***** type view showing the single type a-Si solar battery created by the doping technique of this invention.

[Drawing 5] It is the outline block diagram showing an example of the roll-to-roll equipment incorporating the doping system of this invention.

[Drawing 6] It is the ***** type view showing the tandem-die a-Si solar battery created by the doping technique of this invention.

[Drawing 7] It is the ***** type view showing the triple mold a-Si solar battery created by the doping technique of this invention.

[Drawing 8] It is the ***** type view showing the polycrystal Si solar battery created by the doping technique of this invention.

[Drawing 9] It is the ***** type view showing a-Si TFT created by the doping technique of this invention.

[Description of Notations]

101 Chamber

102 Vacuum Pump

103 Anode

104 Cathode

105 Sample

106 Heater

107 Plasma

108 Power

109 Target

110 Bomb

111 Mass-Flow Controller

112,113 Light source

[Translation done.]